UNIVERSIDADE AUTÓNOMA DE LISBOA

LUIS DE CAMÕES

Departamento de História

Tese de Doutoramento em História

Conservação de Materiais Orgânicos Arqueológicos Subaquáticos

(Conservation of Underwater Archaeological Organic Materials)

Tese apresentada para a obtenção do grau de Doutor em História

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Junho, 2013

ACKNOWLEDGEMENTS

The work presented here would not have been possible without the help and collaboration of a group of people I would like to thank. To start with, the members of my committee, Prof. Adolfo Silveira Martins and Prof. Donny L. Hamilton. They kindly accepted me as their student and since then have been most supportive and helpful.

Enough cannot be said about the help I received from Helen Dewolf, at the Conservation Research Laboratory, and also Dr. Wayne Smith. They were willing to teach me everything that they knew, get me any supplies and samples that I needed and they were always there to check my work and to guide me when needed.

Deep gratitude is reserved for *Fundação para a Ciência e Tecnologia* (SFRH / BD / 49007 / 2008), to Dr. Jorge Campos of the *Câmara Municipal de Portimão*, without whose interest in supporting me, this research would not have been accomplished.

A thank you to Madalena Mira, *Universidade Autónoma de Lisboa* Library Director, and to Doctors Mike Pendleton and Ann Ellis from the Microscopy & Imaging Center, at Texas A&M.

Another word of appreciation to Dr. Adolfo Miguel Martins and Dr. João Coelho from DANS, for the enlightening conversations and help during the research.

An especial thanks to Tiago Fraga as without his believing in me, his support and friendship, this study would never have happened. Also to my friends Paula Costa, Vanda Germano, Jorge Baptista and Maria João Reis Rocha who always gave me the encouragement I needed. To Luísa Veloso, who opened my eyes, and to Catherine Sincich (TA&MU).

Finally, to my husband, António Machado, who went with me on this journey, and to my family for their incredible support.

ABSTRACT

The main proposal of the thesis "Conservation of Underwater Archaeological Organic Materials" is to present to archaeologists and archeology technicians, in an understandable way, the principles and procedures of the conservation of underwater archaeological organic materials, thus maximizing the efforts and results of the preservation of underwater cultural heritage.

The aim to this study is, also, to define new interventional procedures concerning the conservation and restoration of underwater archaeological heritage and combine these with information and training.

In this sense, after the characterization of the type of organic materials, commonly found in underwater archaeological sites, the identification of conservation status is followed. From this, the causes and their levels of degradation are recognized and understood. This step provides information and is also essential to ensure the future integrity of organic archaeological remains.

From critical research-based methods and laboratory tests, specific methodologies are presented for the preservation of organic materials from underwater contexts, which can be implemented by the various technicians and experts in the field of underwater archeology and thus contribute to the safeguarding of heritage.

Key-words: underwater archaeology; organic materials; state of conservation; methods of conservation.

RESUMO

O objetivo principal da tese "Conservação de Materiais Orgânicos Arqueológicos Subaquáticos" é apresentar a arqueólogos e técnicos de arqueologia, de forma simples, os princípios e os procedimentos da conservação de materiais orgânicos de proveniência subaquática. Maximizando, assim, os esforços e os resultados da preservação do património subaquático.

Pretende-se, igualmente, com este estudo definir novos procedimentos de intervenção relativos à conservação e restauro do património arqueológico subaquático e com estes aliar a informação e a formação.

Neste sentido, após a caracterização do tipo de materiais orgânicos comummente encontrados em sítios arqueológicos subaquáticos, segue-se a identificação do estado de conservação. A partir deste reconhece-se e compreende-se quais as causas e os respetivos níveis de degradação. Esta etapa permite obter informação e é também fundamental para assegurar a integridade do espólio.

A partir de uma pesquisa crítica baseada em métodos e análises laboratoriais, são apresentadas metodologias específicas para a preservação de materiais orgânicos provenientes de contextos subaquáticos, as quais podem ser implementadas pelos vários técnicos e especialistas no campo da arqueologia subaquática e, assim, contribuir para a salvaguarda do património.

Palavras-chave: arqueologia subaquática; materiais orgânicos; estado de conservação; métodos de intervenção.

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ABBREVIATIONS

CCI	Canadian Conservation Institute
CNANS	Centro Nacional de Arqueologia Náutica e Subaquática
CRL	Conservation Research Laboratory
DANS	Divisão de Arqueologia Náutica e Subaquática
EDS	Energy Dispersive X-Ray Spectroscopy
ICOM	International Council of Museums
ICOM-CC	International Council of Museums Committee for Conservation
IGESPAR	Instituto de Gestão do Património Arquitectónico e Arqueológico
IPA	Instituto Português de Arqueologia
IPPAR	Instituto Português do Património Arquitectónico
TAMU	Texas A&M University
UNESCO	United Nations Educational, Scientific and Cultural Organization

GLOSSARY

Acid	Compound that gives off H^+ ions in solution.
Base	Substance which gives off hydroxide ions (OH^-) in solution.
Catalyst	Substance that speeds up a chemical process without actually changing the products of reaction.
Centistoke (cSt)	Unit of measure for kinematic viscosity equal to the unit millimeters squared per second.
Concentration	The amount of substance in a specified space.
Cross-link	Bonds that link one polymer chain to another through covalent or ionic bonds.
Cross-linking	Process in which large polymer molecules react with each other to form 3-D nerwork.
Curing	Process that refers to the toughening or hardening of a polymer material by cross-linking the polymer chains; it can be achieved by UV radiation, heat, chemical additives or electron beam.
Fibers saturation point (FSP)	It is the moisture content at which all sites of a cell wall that are able to adsorbed water are saturated. The FSP varies according with the different species of cellulosic materials.
Hydrolysis	The reactions of cations with water to produce a weak base or of anions to produce a weak acid.
MTMS	Methyltrimethoxysilane, an hidrolizable multifunctional alkoxysilane polymer.
Oxidation reaction	A reaction where a substance loses electrons.
Polyethylene glycol (PEG)	Polyether compound.
Silicones	Inert and synthetic polymers, that are heat-resistant and rubber-like.
Silicone oils	Polymerized siloxanes.
Siloxanes	Chemical compounds composed of units of the form R_2SIO, where R is a hydrogen atom or a hydrocarbon group.
Viscosity	Measure of the resistance of a fluid which is being deformed by either shear or tensile stress.

CHAPTER I – INTRODUCTION

1. Background to Dissertation

Conservation work is a specialization and an independent field of study. However, it is clear the importance of the relationship between archaeologists and conservators towards the preservation of cultural heritage. Like archaeology, underwater archeology records the three dimensional structure of a site to reconstitute the sequence of the accumulation of objects and debris. This process looks to obtain an idea, as close as possible, of the conditions and use of objects before they became considered cultural heritage. Nevertheless, particularly in underwater archaeology, the inexistence of a given element does not mean that it did not exist. But rather that factors such as sedimentation, currents, corrosion, marine growth and others did alter the condition of deposits. By employing a wide range of techniques, those circumstances can also be explained by conservation. Based on a scientific approach, conservation can help enlighten features about the materiality of objects, thus providing information to archaeology.

The main problem of underwater archaeological organic materials is their drying, as during this process shrinkage and collapse can occur. In the 1850s, conservation of submerged heritage began at the National Museum of Denmark, with work performed upon wooden objects from a wet archaeological site. At that time, regarding the stability of organic materials, alum was considered the best option.

During the XX century, conservation followed archaeological development. The number of shipwrecks discovered forced new developments in conservation and archaeology. Almost one hundred years after alum treatment was used, it was considered a very hazard procedure in the 1960s and was replaced by others. Thanks to technological and scientific developments, acetone-rosin started to be used for stabilizing small sized pieces. Polyethylene glycol (PEG) has also been used for almost all kind of materials, also being applied as an adjuvant in freeze drying treatments. In recent years, treatments with silicone oils, especially in the USA, and critical drying have begun to be used, with new protocols being introduced worldwide.

In Portugal, despite its maritime history and the importance given to the study of materials recovered from underwater archaeological contexts, the waterlogged organic conservation and restoration still have no systematization or even a program designed for the protection of underwater archaeological heritage. Furthermore, during a lot of archaeological research, artifacts end up suffering hazards that undermine their integrity and can even cause irreversible damage, a situation that has consequences for their historical value and simultaneously limits future research.

Since the 1970s, perhaps thousands of underwater archeological artifacts have been found in the Portuguese sea or on the shore, either by fishermen, interested collectors, divers or local people. From this period until 2007, a series of government decrees stipulating the rules of Portuguese underwater archaeological activity were created along with governmental institutions. However, a few of these artifacts have been treated only in the last two decades, meaning that many others have been irretrievably lost.

Likewise, we find an analogous situation with regard to academia. Despite the number of reported underwater remains and the need for their preservation, the information needed to train human resources in conservation is only now starting its first steps at an academic level. Furthermore, in general, knowledge is acquired through the study of scarce scientific literature, and practice of these same notions is often developed in situations of effective safeguards.

These circumstances proved in reality a common methodology with very few scientific developments in conservation and restoration of underwater archeological materials in Portugal. That is, even with the development of a government department dedicated to underwater archeology or the ratifying of the UNESCO Convention On The Protection of The Underwater Cultural Heritage (2001)[1] at a national level the implementation of programs related to the protection and conservation of underwater cultural heritage is still lacking. On the other hand, despite the existence of a laboratory for conservation and restoration in the *Divisão de Arqueologia Naútica e Subaquática* (DANS), the repercussions of the scientific results of the work performed by this institution, responsible for the preservation of underwater heritage in Portugal, are practically nonexistent.

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[1] Published in Portugal's official newspaper Diário da República, I SÉRIE N.º 137 de 18-7-2006. Dec. Do Presidente da República, n.º 65/2006, de 18 de Julho.

2. Definitions

Artifacts and non-artifacts play an important part in the archaeological record. The fact is that many times the material culture can offer precise information about a historical and social context, as it serves as evidence of the past. Therefore, considering its importance in this dissertation, regardless of its nature, size, or underwater environment, we are going to use these terms: artifacts, objects and/or materials, to define the source of our study of underwater archaeological organic materials.

Considering the United Nations Educational, Scientific and Cultural Organization (UNESCO) description of underwater cultural heritage, as “having a cultural, historical or archaeological character which have been partially or totally under water, periodically or continuously, for at least 100 years”[2], we are going to use the general term underwater to describe submerged environments, such as sea, estuaries, and rivers, beneath sediment or upon this; and the expression underwater archaeology to define the scientific investigation towards historical knowledge, regardless of the aspects of the research field, nautical or marine.

In a few decades, archaeology has enlarged its field of research and with it increased the amount of cultural heritage evidence, and in turn, raised the need to ensure its durability, integrity and access. Conservation offers the best possibility toward durability and integrity, and toward stability and access. In this context, the terms conservation will be used in this dissertation to described stabilization treatments, and preventive conservation to refer to all measures related with maintenance and access.

In the context of underwater archaeology another term has arisen: waterlogged, meaning wood “at or near its maximum water content”[3], we are going to use this expression to identify every organic material that has its maximum water content.

Finally, conservation concerning organic waterlogged finds from archaeological wet sites, besides describing the measures taken for general preservation, will be used to describe all physical and chemical measures taken during the stabilization of materials. This is the same notion given in 1972 by UNESCO, describing the effective and active

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[2] UNESCO - Convention on the Protection of the Underwater Cultural Heritage. Paris: UNESCO, 2001. Article 1.

[3] SKARR, Christen - Water in wood... p. 84.

measures that can be taken to ensure the identification, protection, conservation, presentation and transmission of heritage[4].

3. Delimitations

The underwater environment presents conditions that allow high rates of material conservation, fostering archaeology to interpret it in a historical sense, regardless of the environment in which the material is found: sea, river, lake or in a damp area on land. Therefore allowing the retrieval of information at a historical and social level as never before. Despite the multiple nature of material found in an underwater environment, this dissertation is focused only on organic material, regardless of its underwater contexts. We chose this as an object for research due to the fact that this is the most found in underwater archeological sites and also the most perishable, if not well conserved. Hence our interest in its presentation explaining the processes associated with its conservation, both in terms of *in-situ* preservation and laboratorial treatments, seeking to raise awareness of archaeologists to the threats leading to the destruction of underwater archeological deposits.

4. The dissertation aims

The work now presented at the *Universidade Autónoma de Lisboa*, for a doctoral dissertation in History, aims to investigate which treatment acts better as a stabilizing agent for waterlogged organic materials and which method is easier to perform.

This research also intends to contribute to the understanding of materials and conservations techniques, as well as to present treatment procedures in the most accessible way to different specialists connected with underwater archeology. In most cases , professionals establish the first contacts with deposits, sites and their contents, rather than conservators. The description of a wide range of conservation techniques enables historians, archaeologists and other underwater archeology experts to be aware

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[4] UNESCO - Convention Concerning the Protection of the World Cultural and Natural Heritage, Adopted by the General Conference at its seventeenth session Paris, 16 november 1972. UNESCO, 1972. Article 5.

and better prepared, preventing material destruction or neglect. We firmly believe that underwater archeology will continue to grow and with it the need for cultural heritage care, as Berducou stated: “conservation-restoration is also becoming the indispensable companion of archaeology”[5].

From a baseline study that combines Archaeology and Conservation we hope to raise awareness and lead to more accurate actions, from excavation, through stabilization of artifacts until their display or storage. To achieve this purpose the conservation concepts, theoretical issues and intervention criteria are clear, seeking to define a working methodology that allows the protection of underwater archaeological heritage, in a pragmatic and accessible practice.

In order to address questions raised during the research, namely the effects of treatments, four methods were performed, specifically the removal of iron stains from a cotton fabric, shoe conservation using silicone oils, the impregnation of non degradable wood using silicone oils and silicone oil removal. The first method was developed based on the possibility of using a leather treatment in cellulosic fibers. The second to better understand the silicone procedure. Regarding the last two, they were conducted in order to establish the degree of the impregnation and feasibility of the removal of silicone oils accomplished through the examination and analysis of samples.

Considering this reality, and knowing that conservation methods for organic materials, regarding the use of polymer technology, have been implemented with some success, the author of this dissertation, in a combination of efforts between archeology and conservation, that aims the most for the preservation of underwater archaeological organic materials and based on a critical selection, presents some conservations methods suitable for development by archaeologists.

5. Methods and references

The research methodology developed in this study was based on a scientific approach, at a theoretical and practical level, but is also supported by experience gained through our professional development, which is considered to have an important role.

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[5] BERDUCOU, Marie – Introduction to Archaeological Conservation... p. 258.

The methods developed were based on treatments applied in the conservation of artifacts from wet archaeological sites. The first study performed intended to remove oxides from cellulose fibers. This removal was based on the research methodology applied upon leather by the Canadian Conservation Institute, and carried out in that institute.

To better understand silicone oil treatment and its effects on the shape and dimension of materials, several experiments were conducted. The first was based on shoe and shoe last conservation, which was performed according to the method developed by the Archaeological Preservation Research Laboratory (APRL) and the Conservation Research Laboratory (CRL) at Texas A&M University (TAMU).The results were interpreted based on visual inspection, where the aesthetic was the major parameter.

The second experiment was the impregnation of samples of new wood. In this experiment the penetrating ability was analyzed through Computer Tomographic scanning (CT Scan) available at St. Joseph's Medical Center. The benefit of this research was to compare impregnation according to the nature of each wood and the different silicone oils viscosity, a study which has not been previously done. In addition, others aspects were studied, namely the general aesthetic of samples and a comparative analysis of color, brightness and measurements.

The last experiment was focused on the possibility of the removal of silicone oils and the materials response to this procedure. In this case, samples of treated wood were prepared, according to the protocol used at the Microscopy & Imaging Center, at TAMU, and then analyzed using the Scanning Electron Microscope (SEM) and Electron Dispersion Spectroscopy (EDS) of that Center.

As for the references that had guided the research, considering the fact that conservation within underwater archaeology is a new field, the most known references followed were: Colin Pearson, Conservation of Marine Archaeological Objects, 1987; J. M. Cronyn’s, The Elements of Archaeological Conservation, 1990; Donny Hamilton’s, Basic Methods of Conserving Underwater Archaeological Material Culture, 1996, as well as associated with this Wayne C. Smith’s, Archaeological Conservation Using Polymers, 2003; Wendy Robinson, First Aid for Marine Finds, 1998.

According to the nature of materials, other specific references were also consulted. Excellent sources of information were also the several Proceedings from ICOM Group on Wet Organic Archaeological Materials.

6. Thesis outline

This dissertation is structured into five chapters plus one appendix. In Chapter I the parameters of research are set out, as well as background information, methodology and a review of the literature about the conservation of underwater archaeological organic material. Chapter II presents a brief introduction to the role of underwater archaeology, its emergence and the importance of cultural heritage to historical knowledge, relating it to preservation and conservation. This chapter also presents a brief survey of the underwater archaeology and conservation of waterlogged cultural heritage in Portugal.

In Chapter III general characteristics of organic material are provided, as well as information about its reaction to the environment and other degradation mechanisms, thus explaining the most frequent deterioration phenomena.

Chapter IV provides information about the excavation process within conservation. Through the characterization of changes and according to the specific needs of each element, effective treatments are determined along with information about preventive conservation. This chapter has as its main target specifically those outside the conservation area. Thus, for a better insight into preservation, the values of conservation criteria are also presented, with a particular look into reversibility, demonstrating why a more nuanced approach towards this "paradigm" is needed. This chapter also presents the differences between treatments which are given according to their effectiveness, time spent and cost. At the end, a discussion about the main advantages and limitations of those preservation techniques is outlined

Chapter V is devoted to the presentation of case studies, giving experimental details about two treatments: the silicone impregnation and removal of oxides from a cotton textile. This chapter also provides the analysis of macro and micro effects of silicone impregnation, the observation, analysis and identification of the effects of the removal of silicone from treenail samples and the results of the removal of oxides from the cotton textile.

Chapter VI contains the general remarks about the research done, crossing the practical applications integrating conservation with underwater archaeological practices. An overall discussion of the treatments available for the conservation of waterlogged organic materials is presented. The thesis is concluded by a suggestion of further investigation into silicone oil extraction and the need for continuous collaboration between disciplines as a way to preserve cultural heritage.

CHAPTER II – UNDERWATER ARCHAEOLOGY AND ITS CULTURAL HERITAGE CONSERVATION

7. The development of underwater archaeology

The XIX century consecrated a new perspective of history. In this time of profound changes, man felt the need to know about his past. In Europe the first questions raised were about the origins of civilization, demands that led history to recognize archaeology as an important tool for understanding the past. This was also the time when the study of physical remains began to be systematized, giving rise to the development of modern excavation techniques and later to the interpretation of archaeological contexts[6] allowing an increase in our historical knowledge[7].

In its goal to understand social transformations and their relationships, archaeology is not limited to a type of record, place, civilization, or period of time before or after writing was invented[8], neither is it reduced to the status of physical discovery[9], which would minimize archaeology itself. In the holistic study of the story of mankind, archaeology now has a number of other branches that include, for example, underwater archaeology, or simply archaeology[10].

It is unavoidable that archaeology looks to sources of information such as submerged sites, since from generation to generation people have crossed water leaving traces of their movements. For example, through maritime trade, bonds between cultures were created, economies established, societies formed[11] and people settled on coastal areas. Thus, structures associated with these events like wells, wrecks, crannogs, bridges and harbors[12] are considered as archaeological resources. In general, the term used to define this research is underwater archaeology, but others can also be used to

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[6] HODDER, Ian; HUTSON, Scott – Reading the Past... p. 187-191.

[7] JOHNSON, Matthew – Archaeological Theory…

[8] With the "document revolution", the historical science opening to a new universe of possibilities where the notion of document is enlarged, from the written documents to oral or illustrated documents, and even archaeological excavations, see LE GOFF, Jacques – La nouvelle histoire... p. 38.

[9] HODDER, Ian b) – The Interpretation of Documents and Material Culture… p. 266-281.

[10] BASS, George a) – Archaeology under water... p. 15.

[11] It is thought that in the Middle Neolithic/Early Copper Age marine-estuary exploration was already carried out by groups of people with their own social and cultural identity. Cf. SILVA, Carlos Tavares da; SOARES, Joaquina – Os Recursos marinhos nas estratégias de subsistência de Pré-História...

[12] MARTIN, C. – Archaeology in an underwater environment... p. 17.

better describe the field work, like marine, nautical (archaeology of the ship) or maritime archaeology[13], giving a more accurate idea about the study itself.

Nevertheless, being considered as a "sub-discipline"[14] underwater archaeology uses the same research methodology as archaeology, although there are major differences in the excavation process. Unlike terrestrial archaeology where only a part of a site is excavated, leaving the rest as a "memory" or at the disposal of future interventions, underwater archaeology usually involves the complete research of a site. This approach is due to the new environmental conditions that take place immediately the site is disturbed, causing its degradation. Nevertheless, this does not mean that the information contained in a site is lost forever. This is, overall, a procedure where data is collected, scientific analysis is carried out and, consequently, the archaeological interpretation will add knowledge to history. Thus, like any archaeological process, underwater archaeology can be subject to further analysis, since it is always possible to return to the collected data.

Underwater archaeology has advanced significantly since the first works performed in the XIX century with no proper methodology and even without the direct presence of an archaeologist in the excavation. This resulted in the mass destruction of information, to research where specific methods and technology are used to fully understand how the record was formed and the conclusions that can be achieved by archaeological interpretation.

In the Netherlands, in 1918, during the draining of the shallow bay of Zuiderzee, a large quantity of ships and wooden pieces were found but also lost, due to the lack of preservation treatments. In 1925, on the Italian coast, a group of fishermen found a Roman ship, the *Albenga*. Despite the attempts to proceed with its study and recovery, the structure and its cargo were very much damaged by the research operations.

All the frantic attempts to recover cargo from shipwrecks contributed to the technological development of diving. In the second half of the XX century, after the Second World War, proper archaeological methods were used in underwater

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[13] On the classification of underwater remains here presented see the simplified terminology in MUCKELROY, Keith b)- Maritime archaeology... p. 8-10.

[14] About underwater archaeology been considered as an archaeological "sub-discipline" see MUCKELROY, Keith b) - *Op. cit.* p.4-10; MUCKELROY, Keith a) – Introduction to Maritime archaeology… p. 24-28.

archaeology; this was only possible due to the development of efficient underwater breathing equipment, the *Aqualung*, by Emile Gagnan and Jacques-Ives Costeau[15].

In the late 1950s Nino Lamboglia, Peter Throckmorton and George Bass adapted archaeological techniques to the underwater environment allowing determining the location of finds and registering the site's integrity[16]. As an example, in Cape Gelidonya, Turkey, all the ship and cargo objects were identified, its position recognized through the use of triangulation from fixed points, also surveying grids were used to make detailed scale drawings, and a water dredge or airlift were used to remove sediment according to the depth and the sensitivity of the site.

In 1961, the *Vasa* archaeological research and salvage were planned in detail to maximize the amount of information recovered and to minimize the effects of the drying of the organic elements[17].

Despite all these developments, some research was carried out using exactly the same methods and equipments as for a terrestrial site. In 1962, five boats from the Viking age were found at Skuldelev, in Denmark. Due to the shallow nature of the site (between 50 cm and 3 m) the research team opted to build a coffer dam around the site and water was pumped out, converting it into a land-based excavation[18].

In the same decade, in 1965, the search for the *Mary Rose* began outside Portsmouth, in the south of England [19]. The team started by surveying the area, but it was only with the help of sonar systems, which allowed the detection of a sub-seabed anomaly, that the location of the ship was confirmed. In 1971, the excavation started and water jets, a dredger to help remove sediment and airlifts were used. During the excavations many Tudor artifacts were found and brought ashore, allowing a better knowledge about shipbuilding and life during XVI century in England.

Underwater research is not limited to Europe or the Mediterranean Sea, as in Northern and Central America wrecks of Spanish fleets were found; in East Africa, excavations started with the *Santo Antonio de Tanna*, in 1977; on the Great Barrier Reef, in the 1960s and 1970s, the wrecks of *Batavia*, in Australia, and *Pandora*, in New Zealand were also found.

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[15] *Idem*, p. 14.

[16] VILLEGAS ZAMORA, Tatiana – Corta introducción a la arqueologia subacuática… p. 33.

[17] The background of the ship's history as well as its excavation and salvage are fully presented in Cederlund, Carl Olof - Vasa I: the archaeology of a Swedish warship...

[18] BLOT, Jean-Yves – Underwater archaeology... p. 60.

[19] For the complete story of the *Mary Rose* project and research see MARSDEN, Peter - Sealed by Time…

By that time maritime and nautical archaeology had become academic disciplines, and institutes related to underwater archaeology were founded, at least in Israel and Scotland, later followed by other universities in the United States of America, such as Texas A&M University and East Carolina University[20].

With modern advances, new tools were developed and the specialization of underwater archaeology work allowed access to deep water sites or to other difficult environments. Surveys with magnetometers, the use of other remote sensing devices, such as side-scan sonar, or the Remote Operated Vehicle (ROV), improved record techniques and even conferred a more scientific approach to archaeological interpretation[21].

These are just a few examples of the research carried out and underwater finds discovered between the end of XIX and end of XX centuries. It is important to notice that underwater archaeology techniques evolved rapidly in the second half of the XX century, allowing better scientific research and, by association, led to the need to preserve objects for storage or public display.

8. Cultural heritage and underwater archaeology

The reconstruction of the (subjective) meanings and use of artifacts is a trend related to a particularly intellectual context, archaeological theory and its relationship to practice, in which the influence of the contemporary society is quite important to the production of archaeological knowledge[22]. However, regardless of the theoretical positions, archaeological objects and other archaeological remains are elements with symbolic value able to support memory bonds, capable of connecting individuals and groups, acting as an element of a democratization strategy[23], representing cultural diversity and therefore considered as cultural heritage[24].

Nevertheless, the notion of cultural heritage can be seen in a different way according to the ownership and the political and social period it refers to. In addition, its

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[20] BASS, George b) – The Development of Maritime Archaeology... p.7-8.

[21] BABITS, Lawrence E.; VAN TILBURG, Hans – Maritime Archaeology... p. 339-411.

[22] TRIGGER, Bruce G. - History of archaeological thought… p. 386-483.

[23] Every culture has as its precondition the human society and, conversely, every human society is accompanied by culture. KROEBER, A. L. – A natureza da cultura... p. 245.

[24] UNESCO - Convention Concerning the Protection of the World Cultural and Natural Heritage, Adopted by the General Conference at its seventeenth session. Paris, 16 November 1972. Paris: UNESCO, 1972. Article1

use can vary according to the construction of ideas about identity and what is regarded to be heritage at that moment[25].

Considering that the concept of culture heritage is always developing[26] and also taking into account the historical importance, cultural significance and social knowledge that can be extracted from underwater archaeological contexts[27], it is understandable that cultural heritage also implies underwater archaeological materials.

The importance of this heritage was first recognized by Recommendation 848 as a result of an Assembly Debate, held by the Council of Europe, in 1978[28].

In 1985, this recommendation resulted in the Draft European Convention on the Protection of underwater heritage, which recognized "all remains and objects and any traces of human existence located entirely or in part in the sea, lakes, rivers, canals, artificial reservoirs or other bodies of water (…) shall be considered as being part of the underwater cultural heritage (…)"[29].

Years later, in 2001, the Convention on the Protection of the Underwater Cultural Heritage reaffirms the willingness of the former, defining exclusively underwater cultural heritage as "all traces of human existence having a cultural, historical or archaeological character which have been partially or totally under water, periodically or continuously, for at least 100 years"[30] and discriminating exhaustively all the possibilities of sites and objects. This recognition has another impact as when subscribing to the 2001 Convention, each country has to formulate legal policies towards the preservation of underwater cultural heritage and apply proper actions to ensure access to sites and materials, recognizing also its cultural property[31].

These publications reinforce the notion that underwater archaeology remains are a source for the collective memory, bringing new ideas, meanings and values to society, being able to create a link with the past that should be preserved as an instrument for

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[25] JORGE, Vítor Oliveira – Arqueologia, Património e Cultura… p. 115.

[26] After the "Faro Convention" the concept of heritage has changed extending to new resources, for more detailed information on the dynamic characteristics of heritage, see COUNCIL OF EUROPE – Heritage and Beyond…

[27] MARTINS, Adolfo da Silveira - A Arqueologia Naval portuguesa (século XIII-XVI)... p. 27-28.

[28] COUNCIL OF EUROPE - Recommendation 848 on the underwater cultural heritage, Assembly Debate, Parliamentary Assembly Council of Europe, 1978.

[29] STRATI, Anastasia a) – Draft Convention on the Protection… p. 2.

[30] UNESCO - Convention on the Protection of the Underwater Cultural Heritage UNESCO Paris, 2 November 2001. Article1.

[31] On the enunciation of legal concepts about the meaning of underwater cultural heritage and ownership of the cultural property see STRATI, Anastasia b) - The Protection of the Underwater Cultural Heritage... p. 69-102.

historical, scientific study and heritage[32]. This also means that underwater archaeology has an educational responsibility, to the general public and a specialized one. However, "objects and places are not, in themselves, what is important about cultural heritage (…) they are important because of the meanings (…) and the values they represent"[33]. Thus, the best way to preserve and to reveal their significance is through their presentation in education or cultural recreation, in which their social and cultural meaning must be emphasized. Within this strategy, museums play an important role, revealing the true value of cultural heritage.

Therefore, museums are also responsible for informing and promoting the conservation of cultural heritage. In a deeper sense, this means that these institutions are the legacy from the present to future generations, where history is accessed through enjoyment (in an educational and recreational approach), inducing memory and a sense of community. In this way museums should provide for collections to be displayed, studied, preserved and most of all that the knowledge obtained, from those artifacts, echoes of the past, is disseminated.

Beyond this, museums, through culture heritage, have yet another important role in society as they represent an economic source for the local populace. Museums reflect society's expectations and its changes through their critical facet, so important for the development of cultures. However, they are also able to generate financial income and thus benefit the region in which it is situated.

This is also the case of underwater archaeology museums, maritime, nautical museums or museums with underwater archaeology collections, since they are agents of social and cultural development of their communities. Through exhibitions of underwater materials, the public is exposed to its history, becoming aware of the importance of such heritage and also the risks of losing it. On the other hand, underwater archaeology has always captivated the public with the romantic idea of an adventurous past, a situation quite visible by the worldwide growth in the number of people who visit maritime and nautical museums, and also *in situ* shipwrecks and other historical structures. This means that besides underwater heritage being a public service, it also brings economic benefits to the region where such features are and, at the same time, induces social cohesion, strengthening the identity between communities.

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[32] COUNCIL OF EUROPE - European Convention on the Protection of the Archeological Heritage. Valetta: Council of Europe, 1992.

[33] COUNCIL OF EUROPE c) – *Op. cit.* p. 8.

9. Brief history of waterlogged organic materials conservation

In its research, underwater archaeology has enlarged its fields of exploration and in a few decades studies have multiplied, with the amount of the cultural heritage evidence growing, most of it belonging to shipwrecks.

Usually, a shipwreck contains evidence of the everyday objects used in domestic activities and working tools; data on trade goods destined for markets, in the case of seafaring boats; and traces of the technology used in warships and other vessels, indicating the degree of development of the societies responsible for them. Besides this evidence, high degrees of information can be extracted from an underwater context, if not only the wreck is considered, but it is seen as part of a major system, involving other elements such as coastal cities, harbors, repair yards or markets. Therefore, the data recovered is not just about life aboard the ship, but also about human relations in society, economic contacts and technology.

Another distinctive feature is that these sites tend to be single events in time; the term used for such events is a “time-capsule”, where all objects were deposited at the same time, offering a deposit with a minimum of external interference and, most of the time, with a satisfactory state of preservation, bringing new explanations into the historical and social context. Quite contrary to what happens in land archaeology, where human (re)occupation and post depositional are influenced by natural causes, leading to a mixing and alteration of materials, limiting or complicating archaeological interpretation[34].

All these situations have put pressure on the need to ensure its durability, integrity and access, which can only be achieved through conservation.

Conservation work is a specialization, technically committed to the preservation of cultural heritage. Although it is placed in an independent field of study, it is obviously important for archaeology. Firstly, because archaeology and underwater archeology are irreplaceable moments that once physically started cause changes in the context. Hence, the process of obtaining an idea of the conditions and use of objects means a gain in information but also represents a loss[35] that must be considered. Thus, conservation has a major role in delaying the rate of degradation and protecting and preserving materials. Secondly, besides the changes in the underwater archaeological

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[34] GREEN, Jeremy – Maritime Archaeology ... p. 4.

[35] YOUCENAR, Marguerite – That Mighty Sculptor, Time... p. 214.

site's original characteristics, it is important to understand that the absence of a given material does not mean that it was not present on that site, but rather factors such as sedimentation, currents, corrosion, marine growth and others played a part in its deterioration, circumstances that can be detected and explained by conservation. Furthermore, conservation can also work to enlighten features about the materiality of objects, thus providing information to archaeology and to history. Regarding the words of Hasslöf[36] about the study of maritime past, we dare to say that like other studies such as iconography, etymology and ethnology, so conservation should be regarded as an important axis of archaeology.

The need to preserve and understand the nature of materials emerged in XIX century, and in those days care was concentrated on artworks and buildings. However, in the early years of archaeology as a discipline, the recovery and analysis of material culture turned to other elements such as architectural elements, pottery and metal artifacts. Shortly after 1880, in a burial mound in Norway, a wooden ship, the *Gokstad*, was found and the conservation of archaeological organic materials took its first steps. Years later, in 1903, again in Norway, a clinker built ship, the *Oseberg*, was found and investigated. The particular burial conditions, which prevented oxygen reaching the burial chamber, allowed a very good preservation of the ship and all the associated artifacts. By this time the first scientific methods for treating waterlogged wood were already underway in Denmark[37], where a few years later Georg Rosenberg conducted the first attempts to preserve organic materials by means of environmental control[38].

From then on many other underwater archaeological materials were conserved. In 1925, when the Roman ship, *Albenga* was found, the original idea was to study the vessel and exhibit it in a museum, but unfortunately it was destroyed by fire in 1944.

The most remarkable conservation intervention happened with *Vasa* after its discovery, as due to its good state of preservation it was decided to salvage the wreck and plans were made to do this. In the next years, the ship and its artifacts were treated[39] and a museum around the ship was built.

A similar situation occurred with the *Skuldelev* ships, recognized as important elements for the knowledge of Viking nautical technology. In view of their poor

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[36] HASSLÖF, Olof – *Op. cit.* p. 11.

[37] GRATTAN, David a) - History of Conservation…

[38] CLAVIR, Miriam – Preserving what is valued... p. 16.

[39] BARKMAN, L. – The preservation of the Warship Wasa...

condition, conservation was imperative, so treatments were carried out and a museum was built at Roskilde for the exhibition of the ships.

Another example was the *Bremen* cog which was completely disassembled, treated, reassembled, and displayed in the German National Maritime Museum, in Bremerhaven.

During the foundation laying site preparations for the Stock Exchange building in Marseille, France, a Roman vessel was found, but all the required archaeological studies could not be undertaken on site. The excavation of this merchant ship took less than thirty days: the associated artifacts were collected and catalogued and the remains of the ship were split in two, raised and transported to a shed for the rest of the archaeological studies to determine the ship building techniques and function of the vessel, as well as the conditions under which it sank. In this case, the monitoring and conservation procedures were vital for the success of the research[40].

In 1980, the hull of the *Mary Rose* was salvaged from the seabed, placed on her keel at Portsmouth, where it has been preserved and a museum is being built, expecting to open to the public in May 2013.

Also in Texas A&M University, several artifacts from *La Belle* have been treated, including the hull, which is in the last phase of treatment[41].

In Australia, artifacts and part of the hull of the *Batavia* also had conservation treatment, and after several years of conservation treatment in the Western Australian Museum's Department of Materials Conservation, the remains were rebuilt and exhibited in the Western Australian Maritime Museum.

As for the hull of the *Pandora* and despite investigations referred to that the hull is preserved as a more or less intact structure, the approach was of preservation *in situ*. This was decided due to the extensive costs, and therefore only pieces which had been recovered before this decision was made were preserved and are now on display at the Queensland Museum.

In Portugal some efforts have been made to preserve the *Ria de Aveiro A*, and treatments are still continuing.

As presented, organic materials were systematically found in wet conditions, which indicate that despite the aggressiveness of the underwater environment, this can

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[40] DROCOURT, Danie; MOREL-DELEDALLE, Myriame - The Roman ship of Marseilles… p. 49–53.

[41] On the *La Belle* excavation see BRUSETH, James E.; TURNER, Toni S. – From a Watery Grave… About the conservation of the *La Belle* hull and materials see HAMILTON, Donny L.; SMITH, C. Wayne – The archaeological role of conservation…

slow down the degradation processes, much better than terrestrial environments. Thus, although many objects were lost, many others were recovered. We firmly believe that underwater archaeology will continue to grow, and with it an increase in the need for cultural heritage preservation. Furthermore, in almost every situation there was an evident interest in the presentation of these archaeological remains, beyond research and towards public display patent in the construction of museums capable of keeping and preserving the collections.

10. Survey of the Portuguese case towards the conservation of underwater cultural heritage

Due to its geographical position, its morphology with a very jagged coastline of bays and estuaries and historical record, Portugal is, necessarily, a potentially rich location for underwater archaeological heritage. Sediment and several changes have led over time to a series of coastal orographic modifications. However, this did not invalidate the continuous use of the Portuguese coastline and it is even possible to speak of use continuity, although with different rhythms. Archaeological records attest to extensive activities in these areas, whether related to sea resources exploitation, or ocean or fluvial trade.

Since antiquity, the extensive Lusitanian facade was considered a valuable resource. In fact, the presence of oriental evidence is a solid data regarding contacts between people, serving also as a witness to the sailing tradition beyond the Mediterranean and into the Atlantic coast at least as far as the River Mondego[42]. Atlantic traffic continued throughout the Roman Empire, as well as the use of coastal and estuarine areas. The archaeological repository attests to this by evidence of Roman fish salting factories, together with amphorae producing centers[43], as well as dense settlements located in coastal areas, the lead stock of anchors[44] and wrecks.

After this period and due to the lack of archaeological evidence or other sources attesting to the force of the Atlantic routes, it is inferred that there was a general

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[42] ARRUDA, Ana - Los fenícios en Portugal: Fenícios y mundo indígena en el centro y sur de Portugal (siglos VIII –VI a.C).

[43] FABIÃO, Carlos – Cetárias, Ânforas e Sal: A Exploração de Recursos Marinhos na Lusitânia. p. 55-594.

[44] ALVES, Francisco [*et al.*] c) – Arqueologia de um naufrágio. p. 183-218.

contraction of trade dynamics. The trade decrease is related to the decay of the economic structure, to which is added the invasions, the growing ruralization movement and monetary contraction. It appears that these were the causes of a change in the rhythm of the Atlantic trade, as well as the reasons for "the death of urban centers whose importance depended on contact with sea routes such as *Talabriga*, *Coninbriga*, *Eburovritium*, *Miróbriga* e *Balsa*"[45].

With the Islamic period, coastline navigation experienced a new energy. The trade of goods was the basis of the Islamic economy and thanks to the economic unity of the Mediterranean Sea[46] the urban markets in Iberia were filled with several products imported from the Orient. This implies not only knowledge of the art of navigation and nautical science, but also the ability to maintain a maritime fleet, as well as the existence of ports or anchorages.

This dynamic moment was followed by another, which came from a blend of economic interest, the emergence of a new social stratum, expansionist policies, a new mentality and, again, Portugal's geographical position, which favoured commercial sea travel and exploration.

These maritime activities, intensified with the development of overseas trade, allowed the economic growth of the Portuguese southern and coastal settlements. The seafront was transformed, natural ports were used and optimized, new commercial centers were developed and other related activities appeared. This new dynamic is also responsible for some transformations such as the urban growth of coastal cities, with the population migrating from rural areas to the new urban centers but also the development of *taraçenas*, responsible for shipbuilding activities that reshaped the Atlantic seashore.

During this period all kinds of vessels anchored in ports, from barges used inland or on the coast, to trade caravel ships or galleons used in sea-going trade.

However, neither the coast nor ports were completely safe. The systems of winds, currents and tides, as well as the silting that altered the navigation bar, were a trap not only for vessels in transit but also for ships which were anchored. But the greatest danger lay in their ocean journeys, with the bad weather that vessels were sometimes forced to endure, to which was added overcharging, poor storage of goods, improper performance of the vessels or their poor maintenance, led to all kinds of

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[45] BLOT, Maria Luísa – Os portos na origem dos centros urbanos...

[46] Catarino, Helena - A ocupação islâmica… p. 77; For a summarized approach of this theme see TAVARES, Maria José Ferro - História de Portugal Medievo: Economia e Sociedade... p. 70-73; 108-115.

accidents and shipwrecks. Dramas so common that they ended up in popular imagery, and in the narratives of the *História Trágico-Marítima*.

According to the above it is clear that the vast Portuguese coastline has an undeniable richness at the level of underwater archaeological heritage. These archaeological sites are not only shipwrecks, but also have a wide variety and quantity of port structures and artifacts. Of these, the largest percentage of all findings belongs to organic materials.

Considering these features, the general progress of archaeology itself, the development of underwater archaeology, we can say that the same evolution process presented earlier happened also in Portugal. For example, if "underwater archaeology as a discipline had its beginnings in the 19th century when salvors, working on the then modern shipwrecks (…) came across ancient materials"[47] the interest in this area, at a national level, can be considered as having been initiated with the work of Henrique Lopes de Mendonça (1856-1931) or Quirino da Fonseca (1868-1939)[48]. Although there are differences between both situations (the first is related to the indiscriminate salvage of the occasionally found shipwrecks and the second to the Portuguese interest in understanding the origins of the *Caravela* ship, during the Age of Discovery, and so the research work was not performed in an underwater environment), the subject nevertheless is always related to research into seafaring and its relationship with the sea.

Despite the previous research, we considered the first stage of underwater archaeology in Portugal to have occurred in the 50s and the 70s.

In the 70s, the shipwreck sites of the River Arade were reported by the *Centro Português de Actividades Subaquáticas* (CPAS). However, despite being considered by the local delegate of *Junta Nacional de Educação* a national discovery, and the subject of a documentary for national television which was aired on July 4th 1972 "The Mysterious Ships of the River Arade", no archaeological research or preservation was performed in that period. This can be explained by the lack of an underwater archaeology government program or institution to address these issues, which resulted in the lost of the collected objects.

This period is also characterized by an intrinsic connection with the emergence of sports diving and the discovery of shipwrecks and salvage of finds. In this period only a small amount of underwater archaeological field work was carried out, in

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[47] GREEN, Jeremy – *Op. cit.* p. 5.

[48] MARTINS, Adolfo da Silveira – *Op. cit.*p. 14-15.

contrast to the large quantity of indiscriminate raising of objects conducted by amateur divers. This activity led to an increasing exploitation of the underwater heritage, such as the case of *Cabo da Roca*. The amounts of looting done there was such that it raised public awareness and growing concern about such acts. This concern had evident results judging by the publication of a decree in September 1st [49], which stated that fortuitous findings of archaeological interest were the State's property, and as such had different treatment in regard to the procedures applied to maritime salvage. It also made mandatory the communication of any find to the nearest port office. Furthermore, it established a tripartite committee comprising representatives of the Navy and the State Departments of Education and Finance, which would be responsible for providing advice on all matters concerning underwater archaeological objects.

Notwithstanding the legal efforts the depredations continued. In 1974, Robert Sténuit led a looting expedition on *Slot ter Hooge*, a Ducth East India Company ship, that sank near Porto Santo, Madeira. Based on this event, Octávio L. Filgueiras formed a working group to protect underwater cultural heritage in national waters. Thus, it is striking the appearance, albeit restricted, of a certain awareness of the importance of underwater heritage[50], which led to other situations in the late 70s.

Only in the early 1980s, through the *Museu Nacional de Arqueologia* (MNA) did underwater archaeology take its first steps in an institutional level, with Franscico Alves with the French Ship *Ocean* excavation, in Lagos, and Jean Yves Blot with the galleon *San Pedro de Alcantara* excavation, in Peniche. These two mark the basis of Portuguese underwater archaeology research.

From the beginning of the 80s until the middle of the 90s, the first institutional steps were taken. This second phase is linked to a new development model, based on a highly economic openness and social environment, linked with the entry to the European Community in the 1990s.

In this decade, the *Centro Nacional de Arqueologia Naútica e Subaquática* (CNANS)[51] was created, allowing the beginning of systematic research. In Ria de Aveiro, Francisco Alves uncovered a supposed mid-fifteenth century ship the *Ria de*

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[49] Published in Portugal's official newspaper Diário da República, I SÉRIE N.º 202 de 1-9-1970. Dec-Lei, n.º 416/70, de 1 Setembro.

[50] About this matter see FILGUEIRAS, Octávio L. – Algumas /reflexões para a definição duma política de defesa do nosso Património…

[51] See DEC-LEI n.º 289/93, de 21/08; DEC-LEI n.º 85/94, de 30/03; DEC-LEI n.º 164/97, de 27/07.

Aveiro A[52]. In S. Julião da Barra, Lisbon, Filipe Castro found the probable *Nª. Sª. dos Mártires*[53]. In the south of Portugal, observations, records and excavations were carried out on the French flagship, *L' Ocean*, wrecked in 1759 near the beach in Salema, Vila do Bispo and on the shipwrecks of the River Arade[54].

After these works, others followed from north to south. Furthermore, in this period, the MNA laid the groundwork for an underwater research unit, investing in equipment and infrastructure, staff training, a specialized archive and the start of the Portuguese Underwater Heritage Archaeological Find Chart.

As the years passed, the number of interventions, assessments and heritage rescue field increased, as well as the number of conferences organized by the MNA on nautical archaeology, with the participation of several foreign experts. This environment allowed the appearance in 1991, of the group *Arqueonáutica-Centro de Estudos*. This group had as its main purpose the study and safeguarding of underwater cultural heritage, which, in conjunction with the MNA allowed the development of research in this area[55].

However, in 1993, with the publication of a new decree, underwater archaeology suffered a setback[56], since the new legislation fostered the commercial exploitation of underwater archaeological sites. Only a year later this decree was revised, giving more importance to the jurisdiction of the National Defense and Sea Ministries[57].

Present legislation, dating from the last decade of XX century, replaced the 1993 act with a new form of intervention in heritage[58]. From that time on, any activity carried out on underwater cultural heritage archaeological has to be of a scientific endeavor, with any destructive or intrusive practices that could damage underwater cultural heritage and its surrounding areas prohibited. The law also specified the rights of fortuity friends, giving a financial incentive based on the find's historic importance. It was believed a major public announcement of finds would result in the better

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[52] ALVES, F. [*et. al.*] a) - Ria de Aveiro A: a shipwreck… ; ALVES, F. [*et. al.*] b) - The remains of the hull of Ria de Aveiro A... ; ALVES, F.; RIETH, E. - Ria de Aveiro A'99...

[53] Expo'98 Pavilhão de Portugal [org.] – Nossa Senhora dos Mártires...; CASTRO, Filipe d) – The Pepper Wreck…

[54] CASTRO, Filipe c) - The Arade 1 Ship…

[55] To better understand the aim and work of this association see CASTRO, Filipe a) – Arqueonáutica…

[56] Published in Portugal's official newspaper Diário da República, I SÉRIE-A N.º 196 de 21-8-1993. Dec-Lei, n.º 289/93, de 21 Agosto.

[57] Published in Portugal's official newspaper Diário da República, I SÉRIE-A N.º 75 de 30-3-1994. Dec-Lei n.º 85/94, de 30 de Junho.

[58] Published in Portugal's official newspaper Diário da República, I SÉRIE-A N.º 146 de 27-6-1997. Dec-Lei n.º 164/97 de 27 de Junho.

preservation of the historical memory and scientific information of Portuguese archaeology[59].

Again, this was possible due to a favorable political situation, the same one that allowed for the creation of the *Centro de Operações de Arqueologia Subaquática* for the Expo'98 World Fair held in Lisbon, which provided public awareness with the exhibition and publication of some work done in this scientific area.

In the same year, and for the same purpose IPA and CNANS were established. The creation of CNANS institutionalized underwater archaeology and the development of underwater archaeology enabled the development of high quality projects, such as the *Ria de Aveiro A* and *Ria de Aveiro B*, including the excavation and conservation of retrieved artefacts. CNANS also furthered its connections through cooperation protocols with national and foreign institutions, as in the case of municipal museums and foreign universities such as Universidade de São Paulo, Brazil, and Texas A&M University, USA, for the research in the River Arade, for example.

In 2007, a new change came in legislation and public administration was restructured: IPA and IPPAR were merged into IGESPAR[60]. After a decade of existence, by IGESPAR ordinance of March the CNANS was downgraded to DANS [61]. Despite the change, its scope was maintained, the protection and study of underwater archaeology continued, as well as the continuation of the Portuguese Underwater Heritage Archaeological Find Chart.

The national protection of the endeavor of underwater cultural heritage had setbacks and developments in accordance with social and political dynamics, with a notable growth in recent decades. Although if it is considered that most of the results obtained were summarized in published works, for a specialized audience, and that the effective exhibition of cultural heritage in public display has been scarce, it seems that in that respect more substantial work is required.

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[59] *Idem*.

[60] Published in Portugal's official newspaper Diário da República, I SÉRIE N.º 63 de 29-3-2001. Dec-Lei n.º 96/07 de 29 de Março.

[61] Published in Portugal's official newspaper Diário da República, I SÉRIE N.º 64 de 30-3-2007. Portaria n.º 376 de 30 de Março.

11. Discussion

The research carried out on an underwater archaeological site or materials brings us unprecedented revelations about the past. This historical knowledge is possible to achieve through an interpretative analysis, which is inserted in a particularly spatial, temporal, cultural and social situation that can respond to questions put by history and/or archaeology record.

Underwater artifacts and structures are not classified as heritage only by the excavation exercise or just by themselves. Their surroundings, that is, the context also plays an important part, since certain aspects of the objects are not comprehensible unless the object is reinserted in its original context[62]. This means that to be able to fully present these elements in a coherent dialogue and to be able to proceed with their preservation and conservation, museums need to have access to the archaeological information about the surveys. The work done by conservation is fundamental to the preservation of cultural heritage, but is not an end in itself: it also helps to clarify some features which could contribute to archaeological study and, thus, to have a cultural role in society.

Finally, underwater archaeology cannot be mistaken with treasure hunting, antiquity activity or any other commercial exploitation; rather it is an important research activity where the most value comes from data and its contribution to the understanding of history. Without this responsible approach only a small amount of selected objects of outstanding value (most of the time commercial), would probably receive proper care, while a larger quantity of records, objects, materials and structures, also with value, that is cultural value, would be lost.

The cultural relevance of historic shipwrecks, underwater structures, or underwater archaeological heritage become even more important if archaeology and museums are able to use them, in a recreational way, to play an educational role, captivating the audience with the historical facts and raising awareness of these resources.

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[62] BERDUCOU, Marie – *Op. cit.*p. 256.

CHAPTER III - ORGANIC MATERIALS ANALYSIS

In underwater archaeological excavations, organic materials are often not recognizable. The degradation factors that artifacts are subject to induce changes that occur to their properties, changing their structure, either physically or chemically. This condition may cause a misinterpretation of the artifact, and also generate serious doubts as to the preservation treatment to develop, which is why it is so important to understand the processes that lead to these changes.

This analysis assumes that the mechanisms and deterioration rates of underwater archaeological heritage involve parameters related to the organic nature of the elements and extrinsic factors, such as the environment surrounding the material (pH, moisture level, degree of hydration, temperature, pollution, soil type, conditions of burial, etc.) resulting in a specific state of degradation, thus the decay process does not occur in an isolated form. In addition, if artifacts degrade in a particular manner it indicates a certain type of manufacturing technique or a specific use or wear. This knowledge allow us to understand abrasions, distortions, discolorations, uses, damaged areas and may also contribute to the preservation, display or proper storage of artifacts.

12. General properties of organic materials

The materials of an organic nature are diverse, ranging from wood, leather, tissue (animal and plant), bone, including horns or even might be hair or tortoiseshell. The reason they are classed together is because they all contain carbon, hydrogen and oxygen in their composition, in a long molecular chain, which forms polymers. These polymers are formed by chemical bonds (covalent bonds[63]) that are established between other small structural units, called monomers. These molecules bind to each other forming chains rising to specific proteins.

The polymers of animal origin are proteins, also called fiber protein. These proteins arise from a repeated sequence of the natural bond that occurs between twenty amino acids[64]. This originates in different elements such as collagen (leather, skin, bone

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[63] Chemical bonding that occurs between atoms, it is characterized by the sharing of one or more pair of electrons, causing an attraction between them, which shows the union of the molecules.

[64] RODGERS, Bradley A. - The Archaeologist's Manual for Conservation... p. 322-324.

or antlers) in which the protein is deposited outside the animal cell[65]; keratin, if protein is deposited in the cell interior (hair, horns, wool, shell, beaks or claws); and fibroin.

Regarding the cellulosic materials, they are composed of polymers, based on sugar (carbohydrates), in which cellulose is the main polymer (being the glucose the only existent monomer). Nevertheless, others elements can be found to a greater or less extent, such as lignin, hemicelluloses and/or pectin.

Despite the polymeric formation of these materials being common, it is important to understand that they have differences in their specific structure, which mean different solubility[66] and degradation response. Regarding solubility, and although this is a spontaneous reaction common to all polymers[67], the dissolution of materials depends not only on their type and molecules, but also on external causes such as the pH (Potential Hydrogen ion or hydrogen ion level), saline content and temperature[68]. Furthermore, each of the materials is associated with a manufacturing technology, as well as a specific use, which can lead to some changes, both in terms of its conservation status and its preservation treatment[69]. To these circumstances we must add the fact that materials may have already suffered chemical changes, caused by the entry in balance with the environment to which materials remained subjected to throughout their lives[70].

12.1. Leather, skin, bone and ivory

Leather, skin, bone and ivory are frequently found in underwater archaeological contexts. This is due to their importance as merchandise[71] and also because of their use

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[65] *Idem.*

[66] In an underwater context the water molecules (solvent) are absorbed by the polymer (solute); the water molecules push the solid solute, resulting in an increased mass and volume and, after a certain time, a change in the spatial arrangement of the polymer chain, which begins to acquire a greater mobility, spreading slowly in to the solvent, ultimately forming a homogeneous solution, i.e., a dissolution of the polymer.

[67] Since all these polymers possess hydrogen bonding water is easily absorbed by them.

[68] CRONYN, J. M. – The Elements of Archaeological Conservation... p. 239.

[69] FLORIAN, M.-L. E. a) - Deterioration of organic materials... p. 22.

[70] PLENDERLEITH, H. J.; WERNER, A. E. A. – The Conservation of Antiquities and Works of Art... p. 1-3.

[71] As an example of the importance of the leather trade, we quote the royal letter of D. João II, in which he clarifies that no one else could do the transportation of such material except the royal house or his cousin the Duke of Bragança, see BARROS, Amândio Jorge Morais - O Porto e a construção dos navios... p. 135.

in daily life, since these materials were employed in the making of a variety of items including tools, ornaments and art objects[72].

Despite the differences between these materials, due to their structural nature and composition, they are categorized in the same group, the collagen molecule[73]. This molecule arises from the natural bond that occurs with three amino acids, thus resulting in a repeated sequence of the following tripeptide units: glycine (NH_2CH_2COOH), proline ($C_5H_9NO_2$) and hydroxyproline. The first amino acid gives flexibility to the chain and is in greater proportion (30%) than the other two (10%). This ensures the molecule resistance to heat or chemical denaturation[74]. These elements, linked by covalent bonds will form the polypeptide chain, which has a helical structure. In turn, these three chains intertwine to form a triple helix, which is naturally oriented, giving rise and links between fibrils, forming fibers[75]. It is this form of organization that is responsible for a high degree of distension without chain damage.

In the case of hides and skin the links between fibrils vary in thickness forming three distinct histological layers: the epidermis, the dermis and the hypodermis. The first is the outermost layer of the skin, composed of four to five layers, the cornified layer (*stratum corneum*), the translucent layer (*stratum lucidum*), the granular layer (*stratum granulosum*), the spinous layer (*stratum spinosum*) and the basal or germinal layer (*stratum germinativum*). The second consists of connective tissue, divided into two areas, the papillary region and the reticular region, located in a deeper area; and the hypodermis. Finally, there is the lowermost layer which comprises adipose tissue and areolar tissue.

That is, *in vivo*, the thicknesses of these fibers increase gradually from the area of hair to the adjacent area, to the muscles of animals. In addition to these differences in thickness, there is another related to the direction of the fiber growth, which is that the development of fibers is not analogous to the full extent of the animal, ranging from the

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[72] During the Portuguese Overseas Empire many “exotic” objects arrived in Portugal from Asia: ivory chests, lacquered furniture with mother of pearl, leather chairs, ivory fans are just an example of these. GSCHWEND, Annemarie Jordan - Os produtos exóticos da carreira da Índia… p. 123-141. Other example are the leather pieces found during the excavation performed in *Nossa Senhora dos Mártires*, see ALVES, Francisco [*et al.*] c) – *Op.cit.* p. 191.

[73] Also called tropocollagen molecule.

[74] Changing of the structure due to the heat, pH variation and the presence of organic solvents, whether or not irreversible.

[75] HAINES, B. M. – The fibre Structure of leather... p. 525-538.

animal back to the belly and head. These differences are even more significant between different animal species, because each of them represents a specific pattern of fibers[76].

Parallel to the study of these features appears the need to understand tanning, because this operation often causes changes in the fiber structure. Tanning is a process through which the material putrefaction is prevented, enabling other characteristics such as flexibility or resistance, according to the intended final result.

There are several types of tanning agents and various forms of tanning. The oldest and most common tanning is smoked vegetable tanning followed by mineral tanning and lastly, oil tanning.

Smoked vegetable tanning is based on the chemical action of polyphenyl mixtures, resulting from the application of vegetable tannins upon the fibers and despite the fact they establish relatively weak links, they are irreversible.

Mineral tanning is a process applied since antiquity in which alum[77] is applied to the skin, thus establishing chemical connections between this mineral and the existing molecules.

The oil tanning method derives from the oxidation of aldehydes. In this process oils are mechanically applied to dried hide until all the moisture has been replaced by this substance. This tanning can be removed by water immersion.

Another leather component is water, which varies between a “range from 62 and 80% of dry weight”[78] according to the species, diet, age or sex of the animal.

Water may be present in two forms, as an integral part of the collagen structure or as "free water. The first cannot dissolve electrolytes, since it does not move by osmosis or diffusion. "Free water" is bonded to the hydrogen and the fiber surface by weak forces (described by Van der Waals equation) and whose coefficient depends on the existing level of relative humidity. If there is water loss the intermolecular structure is changed irreversibly, becoming a hardened mass. With the loss of "free water" the structure becomes more rigid since the polymers have less mobility. However, they also decrease the probability of oxidation or hydrolysis reactions.

As for bones, teeth or ivory the collagen found in them is exactly the same protein as in skin or leather and the difference is an inorganic deposit of hydroxyapatite

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[76] *Idem*, p. 11-21.

[77] The mineral tanning, using basic salts of chromium or the use of enzymes only appeared in the nineteenth century, a period of great development in chemistry, considering that fact that these kinds of tanning leather are not usually present in an underwater archaeological context, thus we will not proceed with the process explanation of it.

[78] FLORIAN, M.- L. E. a) – *Op. cit.* p. 41.

formed around the fibers. Depending on the existing percentage of each of these elements we can have ossein (1:2 collagen: hydroxyapatite and 5% water), which is the protein that forms the organic structure of bones, or dentin (1:3 collagen: hydroxyapatite and 10% water), known as a matrix protein of teeth which have different mechanical characteristics thanks to their micro and macrostructure, as well as location[79].

The fact is that these materials are more resistant to underwater environmental conditions, because of the existing high percentage of calcium carbonate and the moderate pH value, which provides good conditions for the conservation of both.

The characteristics presented explain the resistance of some of these materials, allowing them to survive even when subjected to underwater environment conditions. However, if these elements promote their conservation, they can also be a factor of degradation; thus, this is a complex situation, which should be analyzed in all its variables.

12.2. Wool, horn, feathers and tortoiseshell

Materials like baleen, wool, fur and hair, claws, hooves, horns, feathers, beaks, turtle shells, fish scales, reptiles or some parts of fins have a common denominator: a fibrous protein, keratin.

In this protein, the number of amino acids is higher, about fifteen, some of which are sulphurous, such as cysteine ($C_3H_7NO_2S$). The keratin amino acids interact between each other through hydrogen bonds and disulphide bonds, and may have two distinct types of structures: the α-keratin and β-pleated-sheet[80]. The first presents a helical configuration, similar to collagen and can be found in elements such as fur and hair; the second presents a chain of a flat structure, forming a stratified large mass, typical of nails, beaks, feathers or corneal productions. Apart from this difference in molecular arrangement, the variation of the quantity of sulphur must also be taken into account. A high quantity of sulphur creates stronger covalent links of disulphide bonds, resulting in

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[79] There are about seven or eight sequences of amino acid, which means different types of collagen, each one with a specific structure and function. Pollard, Mark A.; Heron, Carl - Archaeological Chemistry... p. 274-275.

[80] Nevertheless there are other important fibrous proteins in which the pleated sheet is present, about this matter see RICARDO, C. Pinto; TEIXEIRA, Artur N. – Moléculas Biológicas... p. 132-137.

the protein's greater insolubility, since there is less available space for these molecules to link up with water molecules[81]. Nevertheless, this protein is very hygroscopic[82].

Other physical and chemical characteristics conferred by the molecular structure, although they depend on temperature and water content, are high elasticity and structural stability, which allow the fiber to return to its original format, an ability known as "memory effect".

In structural terms, the hair cell has three components: the cuticle, the cortex and medulla (Fig. 1). The first is an outer layer formed by cells intertwined and joined by ceramides, whose main function is to protect the cortex. In turn, the cortex is formed by very long and pigmented cells, which are organized in a longitudinal and parallel direction, giving elasticity, strength and determining the greater or lesser degree of hair porosity. Each cell of the cortex (or cortical cells) is presented as a bundle of strings called macrofibrills, which are composed of microfibrils, sealed together by the intercellular cement. Each microfibril consists of eleven protofibrils and each protofibril is composed of molecular keratin chains. Finally, the medulla located in the central region of the hair and responsible for rigidity of this, is composed of anucleate cells containing lipid and pigmented granulations[83].

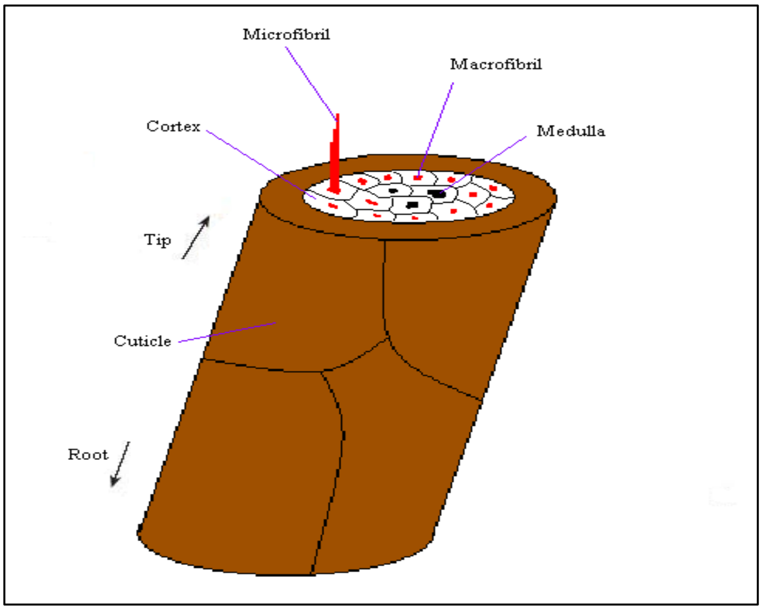

Figure 1 – Hair Structure.

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[81] In the case of a rhino horn its fibers contain fewer sulphur bonds, so they absorb more water (about 49%) if compared to the mane of a horse with the highest number of disulfide bonds, thus absorbing less water (about 33%). FEUGHELMAN, Max – Mechanical Properties and Structure of Alpha-Keratin Fibres… p. 107.

[82] SPEI, M. – The microfibrillar swelling of α-keratin... p. 507-508.

[83] Medulla patterns can vary according to each specimen, so each one has its own characteristics. COOK, J. Gordon – Handbook of Textiles Fibres... p. 98-102.

The corneal structures can be of various types depending on the species. In the case of ruminants, a hollow keratinized epidermis that covers an osseous projection of the skull in lamellar layers with anisotropic properties[84], or as a whole of cemented dermal papillae that form a filament keratinized in the form of hair and with no connection with the skull, such as rhino horns.

In the case of tortoiseshell, they present dermal body plates, covered with horny shields of epidermal origin. In this situation the cells are filled with keratin fibrils and an amorphous matrix.

Reptiles are not much different, with the transversal and longitudinal scales produced by the epidermis, which is mostly made of keratin. These animals may have also developed horny shields.

Feathers are epidermal growths, horny like, consisting of dead cells, keratinized and impregnated by mineral salts such as calcium carbonate and tricalcium phosphate. These develop from epidermal structures, of follicles similar to the fur of a mammal or the scales of reptiles. The basic elements of a feather are: calamus or pipe, rachis, beards, barbules and barbules. The calamus, which grows with a local dermal papilla, is the hollow, smooth part of the feather, is endowed with two holes (umbilicus), one lower and one higher. In the distal prolongation of the calamus arises rachis, the axis from which the beards develop laterally. Beards are thin and narrow blades, in which the barbules are. The last are provided with barbicels in a hook formation that when interlocked with proximal beards, give the whole its consistency. In the region of the upper umbilicus a vexil may develop[85].

Another example is the whale's beards which are long flexible plates of keratin arranged in two rows in the upper jaw of the whale of the *Mysticeti* sub-order. These plates are a modification of the epidermis and, in addition to keratin, contain small amounts of minerals such as hidroxipatite, magnesium, copper, boron, iron and calcium.

Because all these elements are so resistant, it is possible to find them in an underwater archaeological context. However, since keratin is also highly reactive we can expect some differences in its looks and structure.

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[84] Characteristic in which certain physical properties vary according to the direction.

[85] It is possible to find a very good explanation about feather structure in Silva, C.M. – Guia do/a Professor/a...

12.3. Silk

Silk tissues are mainly composed of fibroin. Although few cases of silk elements appear in an underwater context[86] as it was always a valuable merchandise and there are several references of their transportation by sea[87], they are worth mentioning.

Natural silk is made of two main constituents: the fibroin (75%) and the sericin (25%), which are fibrous proteins secreted by *Bombix mori*, aka silkworm silk, or by *Antheraea pernyi* and *Antheraea Mylitta*, wild silkworm silk.

The fibroin is composed of polypeptide chains of neutral amino acids arranged in a β-pleated sheet, with crystalline and non crystalline areas[88]. The crystalline areas have large amounts of amino acids and glycine, maintained primarily by Van der Waals forces that are responsible for the physical strength, while the amorphous zones are responsible for the elastic properties of this protein. However, both the resistance and the elasticity of a silk string also depend on the percentage of water present in its structure. Fibers with low water content are stiff and strong, but break more easily in tension, and the fibers with high water content can expand substantially its original length. Sericin is a protein mainly formed by amino acid residues with polar groups. However, when silk fibers are being prepared, i.e., being degummed with hot water, this protein is eliminated, which means that it is very water soluble.

12.4. Wood and other cellulosic fibers

Wood, rope and fabrics are the most commonly found in underwater archaeological sites. In (almost) all of these contexts we can find wooden materials from structures such as ships, pier poles, through articles of common use, such as spoons, baskets, trunks, or work devices like cables or ships sails made from fabrics. Despite being morphologically different, they are all cellulosic materials, and to understand their

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[86] JONES, Mark, ed. - For future generations…p. 1

[87] *"Um batel grande e largo que, toldado/Vinha de sedas de diversas cores/Traz o Rei de Melinde..."*, CAMÕES, Luis de – Lusíadas. Canto II, 94. p. 122.
"When the Madre de Dios with her cargo was captured by the English off the Azores in 1592: the principall wares after the jewels consisted of ... silkes [being] damasks, taffatas, sarcenets, altobassos, that is, counterfeit cloth of gold unwrought China silke, sleaved silke, white twisted silke (...)" SCOTT, Philippa – The book of Silk... p. 168.

[88] VALLUZZI, Regina; [*et al.*] – Silk... p.166.

degradation and be able to outline a treatment, it is important to understand their phytotomy.

Related to the type of plant, large-sized or not, each one has a specific structure and organization. Common to all of them is to form a complex system in which the fibers are attached to natural resins and gums, which run through roots, stems and leaves. The fibers act as a semi-rigid protection, giving tension and strength to the cells and the whole plant, allowing cells to expand and deform according to the needs of growth. They also provide a passage of key materials for plant development. Within these systems arise various substances such as organic and inorganic components, which are physically and chemically combined in the construction of each plant species, i.e., the distribution pattern. The concentration and the proportions of these elements differ according to the natural needs of each plant. However, the cellular structure is similar, their main components being cellulose, hemicelluloses and lignin.

All these compounds have a major impact on the physical behavior and morphology of plants. Cellulose $(C_6H_{10}O_5)_n$, an element found in greater proportion (between 40 and 60%) in the structure of any plant, is a long chain polymer formed by one monomer, glucose, classified as a polysaccharide or carbohydrate. It presents highly ordered regions, or crystalline, which alternate with less ordered regions, or amorphous, being responsible for the formation of linear or fibrous structure[89]. Due to this constitution it has a high tensile strength and is also insoluble in most solvents.

By establishing hydrogen bonds, together with the Van der Waals forces, which occur between the hydroxyl groups (OH) of the different chains of glucose molecules and the adjacent cellulose, intremolecular bonding is induced. In return, this is responsible for the chain rigidity, and intermolecular links, which makes the chains impervious to water and therefore insoluble[90].

The hemicelluloses ($C_5H_8O_4$ and $C_6H_{10}O_5$), are present in a percentage between 15 and 25%, and they are a mixture of polymers of hexoses, pentoses and uronic acids, which can be linear or branched. They are an amorphous linked material with cellulose microfibrils, bringing elasticity to the plant's structure.

With a highly variable percentage of between 15 and 35%, which also varies according to the type of tissue cells and plant species, lignin ($C_9H_{10}O_2$, $C_{10}H_{12}O_3$, $C_{11}H_{14}O_4$) is fundamentally a three-dimensional amorphous macromolecule. This is not

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[89] RAVEN, Peter; EVERT, Ray F; EICHHORN, Susan E. – Biology of Plants... p. 62.

[90] RICARDO, C. Pinto; TEIXEIRA, Artur N. – *Op. cit.* p. 70-71.

the result of a regular process genetically defined, but from casual links of oligomers, which give rise to a non-linear polymer. This is a biological and chemical process that gives the plant's tissue mechanical rigidity, impermeability and resistance to microbial attack.

These three elements, along with pectin[91] and glycoprotein [92]form the plant's cell wall (Fig. 2). This non-branched linear polymer is composed of microfibrils of cellulose. These fibers do not have a defined direction, but are surrounded by a matrix of pectin, hemicelluloses and glycoproteins, mechanically sustaining and protecting the plant cells[93]. It is this element that allows the free passage of water and also provides the resistance to the excessive increase of cell volume by inhibiting excessive absorption of water, which otherwise would cause the cell to rupture. These elements are also the first layers that form the primary wall.

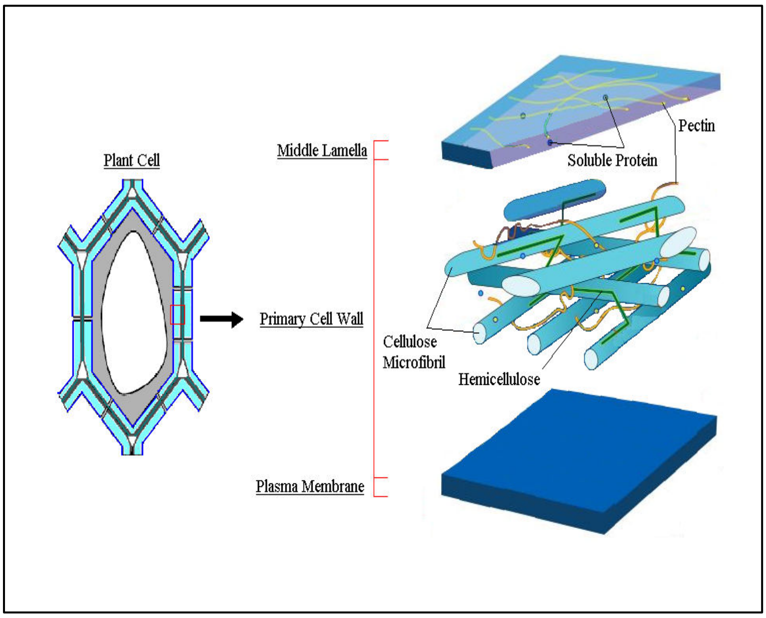

Figure 2– Plant Cell Wall Structure and molecular structure of the primary cell wall of plants.

In some cases, beyond the primary there is a secondary wall. This secondary comes after the development of the primary wall. It consists of three layers (S1, S2 and S3) of cellulose impregnated with lignin, which are deposited inside the primary wall, making the wall thicker (Fig. 3). On this wall, the microfibrils present an oriented

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[91] A polysaccharide polymer consisting of galacturonic acid and galactose, whose branches serve to trap water, making the medium most gelled.

[92] These proteins are responsible for the interaction between cells and for some modifications in those elements.

[93] HALL, J. L.; FLOWERS, T. J.; ROBERTS, R. M. – Plant Cell Structure and Metabolism... p. 350-355.

direction, giving more rigidity to the cell wall. As a form of union between the two walls there is a gelatinous layer, known as the middle lamella, which acts as cement, joining the cells together; it is composed of cellulose fibers intertwined with molecules of pectin and hemicelluloses.

Despite these similarities between the cellular constituents, there are differences between plants in terms of anatomy and morphology. This diversity is due to the specialization of each plant species which has led to a complex variety. Given the large number of the existing differences between plants, a description is beyond the scope of this investigation. However, it is necessary for a better understanding of the status of materials to make a generic species classification.

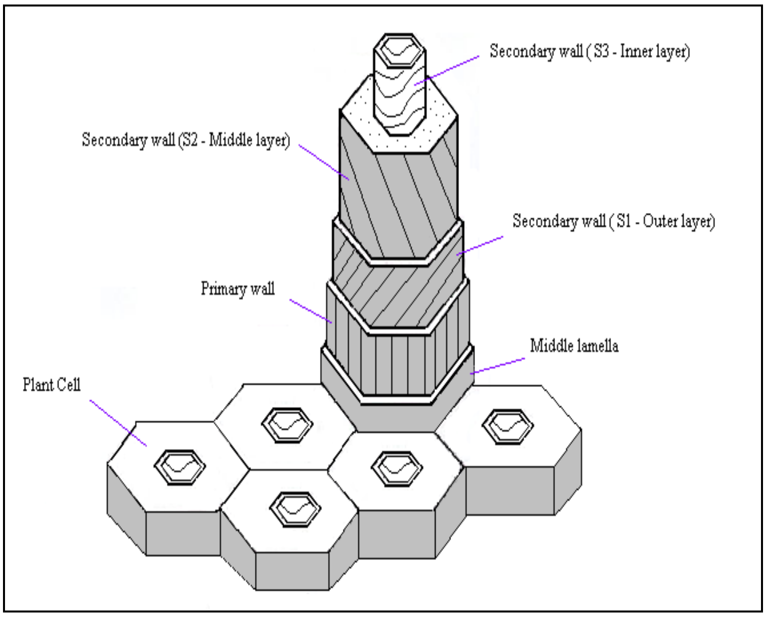

Figure 3 – Schematic disposition of the cell wall layers.

The plant kingdom is divided into: *Thallophyta* (algae, bacteria and fungi), *Bryophyta* (green plants without roots, stems, leaves or vascular system, such as mosses), *Pteridophyta* (vascular plants without seeds, but with storage organs composed of root, stem and leaves), and *Spermatophyta* (plants that produce seeds, higher plants, or plants with roots, stems and leaves, with a vascular system composed of xylem and phloem, which are traditionally divided into angiosperms and gymnosperms).

Considering the characteristics of the last group, the use of such material is the most common. In this set is included the use of fibers originating in the stem such as linen, hemp and ramie; giving origin to seeds such as cotton, from the leaves, such as sisal, or from the fruit, like coconut, but also several wood types.

12.4.1. Flax, hemp, ramie, cotton, sisal and coconut fiber

Flax, taken from the fibrous bark of the plant *Linum usitatissium* L., is the vegetable fiber most found in underwater contexts, because of its range of uses as an exchange commodity[94], thrust force, in the form of sail cloths, or as burlap, an essential element in caulking[95]. The importance of this element was such that since the beginning of the India Route, Santarém and Lamego acted as supply centers of products derived from flax[96], and also diplomatic relations between Portugal and France were encouraged to ensure adequate foreign supplies in periods of scarcity[97].

In structural terms, the liberian fibers have a length ranging from 25 to 120 mm and a thickness between 0.04 and 0.62mm, consisting of several fibrils whose cells have a length between 4 and 69µ and a diameter of 0.008 and 0.031µ. Featuring a continuous tubular, thick-walled, with a narrow lumen and defined, but with bumps, which occur in the transverse divisions, only a slight twist in S is observed (Fig. 4). It presents a rough surface and a linked structure, which favors spinning. In terms of composition it has about 71% cellulose, 25% polysaccharides (molecules that store chemical energy) and 2% of lignin and wax. This last element is very important in terms of the conservation of the fibers, since it acts as a protective agent.

It is an herbaceous plant propagated from seeds which, when developed, are entirely removed from the soil and treated. The process starts by taking off the elements, separating the leaves and seeds from the plant stem or stalk, which is the only part used in spinning. It is followed by maceration through aerobic or anaerobic conditions in which is induced dissociation of the pectic cements and hemicelluloses fiber bundles[98]. This is followed by the separation of fibrils of the parallel bundles through crushing and

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[94] On the use of linen cloths as currency in the period of the Portuguese Overseas Empire see: GODINHO, Vitorino Magalhães b) – Os Descobrimentos e a Economia Mundial... p. 8-9.

[95] Caulking varied depending on the condition of the vessel; the work was to introduce the planking together in tow and pitch, preserving the ship from the action of the water. SERRÃO, Joel; MARQUES, A. H. Oliveira – Nova História da Expansão Portuguesa… p. 170.

[96] Costa, Leonor Freire b) – Naus e Galeões na Ribeira de Lisboa... p. 227-287.

[97] About Portuguese international trade, see among others Costa, Leonor Freire a) - Aspectos empresariais da construção naval no século XVI... p. 295-312.

[98] LANÇA, José Coelho; BAPTISTA, José Manuel – A Cultura do Linho... p. 21.

scutching, resulting in messy and short fibers (tow scutching) and long fiber and parallel (flax scutched). The last step is the separation of the longer fibers, in which the most resistant fibers remain, which will then be spun and woven.

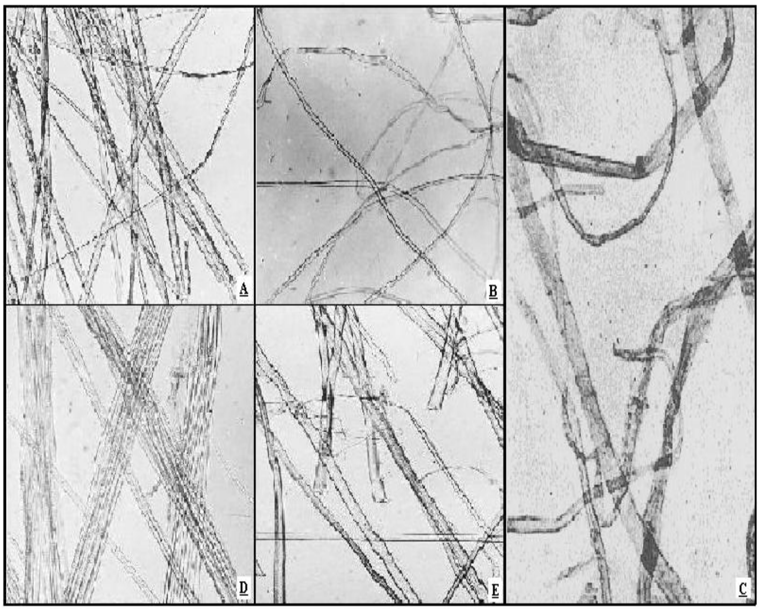

Figure 4 – General aspect of the Plant fibers (A - Agave, B - Cotton, C - Hemp, D - Lin, E - Ramie). (Adapted from CECCATINI, Gregório – Fibras…).

In 1656, under the royal policy of D. João IV for the recovery the Portuguese navy, the cultivation of hemp was established[99]. This material was fundamental for the rigging of vessels, which is also widely found in underwater environments[100].

Obtained from the plant *Cannabis sativa* L., the process of obtaining hemp fibers is similar to the flax procedure. Their cells have a length between 5 and 55mm with a thickness of 0.016μ and produce fibers with a length between 1 and 2m with a thickness of 0.5 to 5mm. One of the characteristics of these fibers is that the first layer presents a maximum of 75% cellulose, 19% polysaccharides and 4% lignin and in the second layer only 30% of cellulose, with the remaining elements having higher values than the first layer. This is why we only use the first layer of fibers, since these contain the highest percentage of cellulose and for that reason are much more resistant. In

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[99] Cf. Regimento que S. Magestade manda que aja na feitoria do linho cáñamo da Villa de Moncorvo, para que os oficiaes della saibão a obrigação, que deuem guardar. [Por D. João IV, em 29 de Agosto de 1656]. Impresso e publicado em Lisboa por António Álvares.

[100] As an example of its use, see the iconography of the Portuguese Empire and the report on the ship *Arade* 1, were some ropes were found, CASTRO, Filipe c) - The Arade 1 Ship…

structural terms the fiber has a cylindrical shape with a longitudinal composition, with a Z twist and some irregularities on the surface (Fig. 4).

Other fibers like the ramie were used as a substitute for linen or woven together with cotton or wool, and were probably used in the production of fishing nets or sewing thread.

Ramie is a herbaceous perennial plant, native to eastern Asia, known as *Boehmeria nivea* (L) Gaudich. The cell diameter varies between 25µ and 75µ, resulting in long fibers (Fig. 4), which are on average 150 to 200mm in length and have a diameter of 0.0034mm[101]. It presents an average of 72.4% cellulose with a lignin content of 0.65% and an amount of hemicelluloses of 14.9%[102].

In its production only the fibers of the stems are used. Extraction starts with soaking the entire plant in water and then going through a series of mechanical processes, to break the structure. The resulting bundle fibers are subjected to a chemical process of bleaching and guillotine cutting, which sets the length of the fibers for further spinning, which can be done in an identical manner to that of linen.

Cotton is able to be found in an underwater archaeological context because it was one of the elements that were for centuries part of the official Portuguese trade, both in Asia[103] and Brazil[104].

Cotton fiber derives from the seeds of cotton, *Gossypium hirsutum* L. The seeds are planted in early spring and harvested between late summer and early autumn, when the cellulose deposited reaches its maximum and the water content its minimum.

Cotton's constitution is formed by unicellular fibers, with a length between 10 and 50mm and a thickness between 0.012 and 0.025mm. These fibers are developed particularly in the outer wall, which has a high cellulose content (94%) with the inner area having the waxes (0.6%), pectic substances (0.9%), protein (1.3%), glucose (0.3%), organic acids (0.8%), oils and cellulose (fewer). After cellulose, wax is the most important element in the cotton fiber, as this is responsible for the control of water absorption by the fiber, and also acts as a lubricant during the fiber spinning process. In

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[101] GODA, K.; [*et al.*] - Improvement of plant based natural fibers...

[102] MOHANTY, A.K.; MISRA, M.; HINRICHSEN, G. - Biofibres, biodegradable polymers and biocomposites...

[103] In Sinde, Sagain, ships were loaded with cotton, from the industrial Cananor, India, arrived good cotton fabrics and from Bengala, Bangladesh, the production was complemented with cotton. GODINHO, Vitorino Magalhães a) – Mito e Mercadoria… p. 403-406.

[104] Under the policy of the Marquis of Pombal, the Brazilian fleet specialized in the transport of goods, such as the cotton that came to Lisbon, from the north of Brazil. CARREIRA, António - As Companhias Pombalinas…

technological terms the first activity is the harvesting; followed by the detachment of the fibers of seeds and other materials; carding; spinning or shredding of the fibers, obtaining parallel fibers, slightly twisted and flattened (Fig. 4), which do not stretch easily, since they are naturally rigid and inelastic[105].

As earlier mentioned, sisal has its origin in the leaves, particularly the ones found in the leaves of *Agave sisalana* Perrine. This plant has large leaves (120cm), which are cut, scraped and beaten to remove the pulp (pectin, hemicelluloses and lignin) that involves "about 1,100 fibers" [106] which each leaf contains. After being washed and dried, the fibers are rolled together to form a continuous string.

The cells of this fiber are slightly cylindrical, stiff and not very flexible, and can be up to 24µ in diameter and 2.5mm in length (Fig. 4). These features combined with the cellulose content "78% by weight of oven dried material"[107] are translated into great physical endurance, since the long fibers have higher energy absorption which is dissipated along its length.

These features allow a good reaction to the demands of physical and tensile strength, hence its use in making ropes and textiles.

As for coconut fibers, there are no references to these findings in an underwater archaeological context. However, occasionally the coconut itself has been found, such as in the wreck *Nossa Senhora dos Mártires*, where it was used as a storage container[108], or also in the archaeological excavations of the *Terreiro do Paço* where several coconut shells were found in association with two piers. This is not surprising when viewing the references to its usage as a caulking material due to its elasticity and incorruptibility at sea[109].

These fibers come from the *Cocos nucifera* L. and are the mesocarp fibrous, which covers the hard and woody shell that protects the coconut. This protection fiber is cut and the pieces are macerated. From this operation the fibers are stripped, washed and dried.

These fibers have a length between 8 and 33mm and a thickness of 0.05 and 0.4 mm. In terms of its constitution, this depends on the type of fibers in question. Thus, in

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[105] However they are still more flexibl than the flax. COOK, J. Gordon – *Op. cit.* p. 72.

[106] *Idem*, p. 28.

[107] FLORIAN, M.-L. E.; KRONKRIGHT, Dale Paul; NORTON, Ruth E. - The Conservation of Artifacts… p. 123.

[108] D'INTINO, Rafaella – Objectos do quotidiano. p. 223.

[109] In our navy, it was used for cable and caulking, and our historians extol the superiority they derived from their elasticity and incorruptibility in the water. DALGADO, Sebastião Rodolfo – Glossário Luso-Asiático... p. 173.

the long fiber, cellulose is the element that is found in a higher percentage (53%), followed by lignin (40.8%) and ash (1.2%)[110], and the percentage of other elements such as pectin or hemicelluloses is quite variable. In the case of short fibers, lignin is present in a larger amount (35-45%) followed by cellulose (23-43%), leaving only a small amount of hemicelluloses (3-12%)[111]. Lignin is also distributed through the thick cell walls, but is virtually nonexistent in the middle lamella, which only has some pectin.

12.4.2. Wood

As stated before, cellulose is a material that is present in a higher percentage in underwater archaeological contexts. Within this category, wood is the element found in greater quantity. This condition is due to its use in construction of structures such as piers, docks, or vessels, and it also emerged as an element used in the making of tools, utensils and various pieces of furniture.

The frequency and its continuous use stems from the fact that it is easy to obtain, and its mechanical and physical characteristics allow an easy transformation and reuse, solving a wide variety of needs.

Wood comes directly from higher plants, trees and some shrubs. It is a heterogeneous material based on a porous and complex system, resulting from numerous capillaries or voids that exist in its composition, which in turn, come from the cellular structure of the plant that gave rise to it. Thus, the details of this structure will vary according to species, depending on whether it is in the group of softwood or hardwoods.

Despite the differences, in all of them can be distinguished macroscopically a concentric orientation in which we find: the heartwood, consisting of the medulla, the core; the sapwood (or alburnum) composed of the cambium (or meristem) and the xylem; and bark, with the living phloem and cork (Fig. 5).

The medulla is the trace in the center of the structure of the stem apex (apical region) from which the stem of the plant develops. It is a structure of small diameter, 1

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[110] SAVASTANO, Holmer – Fibras vegetais... p. 5.

[111] CARRIJO, Osmar Alves; LIZ, Ronaldo Seti de; MAKISHIMA, Nozomu - Características físicas e químicas de substratos à base de pó de coco... p. 163-170.

to 2mm[112]. It is constituted of cells that formed the area of initial growth, marking the growth center of the tree. Medulla cells are progressively younger as it produces its growth.

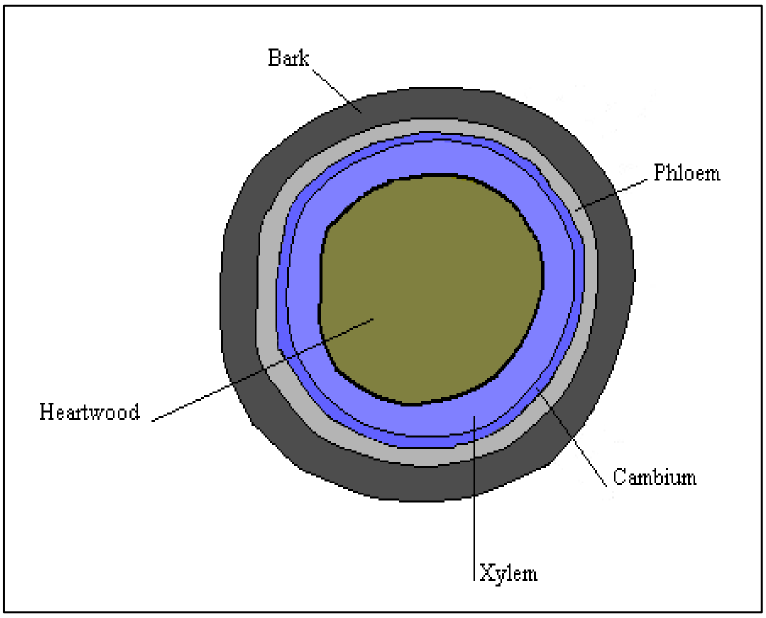

Figure 5 – General composition of a tree trunk structure.

The core is the inner layer composed of dead cells, that is, it is physiologically inactive due to the inactivity of tracheary elements that are no longer involved in conducting water. This element is characterized by a greater natural durability to fungi and insects, due to low water contents and also by the toxic substances it contains[113], but also by a high hardness as compared to other components, so it has basically a mechanical function as a support structure of the plant. It features a dark color, resulting from the oxidation and polymerization of phenolic material.

The sapwood is the area where the physiological activity still remains, that is, an outer layer to the core, lighter in color, where the living cells of the growing tree still process the circulation of water and nutrients between the root and active tissues of the plant. All changes resulting from the thickening of cell walls, which results in turns, from the successive impregnations of lignin, resins, tannins and dyes, are first formed in the sapwood, which later give rise to the growth of the core.

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[112] MELO, Joaquim Roque – Secagem de Madeiras... p. 15.
[113] *Idem,* p.19.

In a cross-section of the stem, there is a thin layer of living tissue, located between the bark and xylem, called cambium. This consists of tissue cells in constant transformation, which allows the modification of starches and sugars in cellulose and lignin. Its growth is achieved by adding new concentric and peripheral layers, the annual growth rings.

In these are reflected the conditions of growth of the tree, narrow and distinct, typical of temperate and cold zones, broad and poorly differentiated, typical of the tropics. The annual rings of growth are in the early years quite wide, but become progressively narrower, since each successive ring is deposited outside the wood which was previously formed, and the rings become thinner as the trunk becomes larger. In each ring two highlighted layers are formed: a light-colored one, with long thin-walled cells formed in the spring-summer, and another dark colored one, narrow cells with thick walls formed during the summer-autumn (Fig. 6)[114].

Finally the bark, whose function is to provide mechanical protection and waterproofing. Here there are two layers: an outer, composed of dead tissue, the cork (rhytidome); and an inner layer formed by living tissue, the liber or phloem.

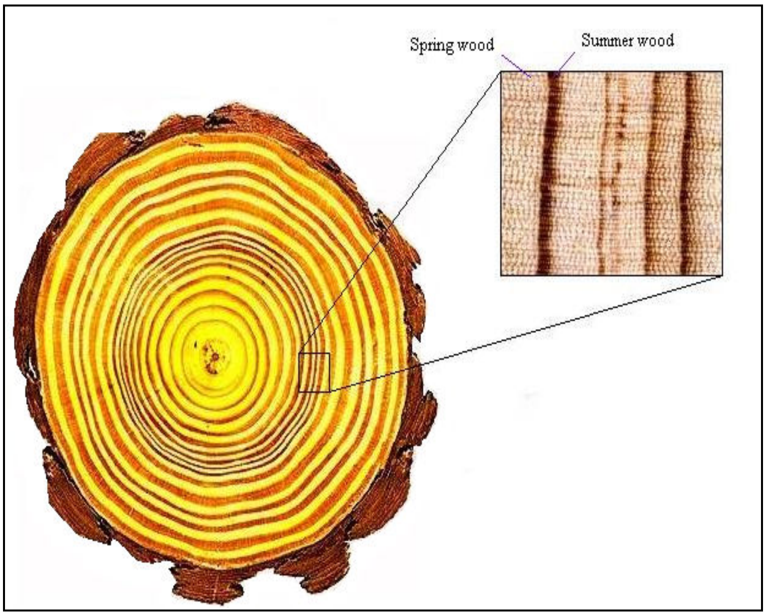

Figure 6 – Growth rings in pine wood.

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[114] The spring and autumn layers will differ according to the tree species and also the nutrients available. FABIÃO, António Manuel D. – Árvores e Florestas... p. 62-72.

In physiological terms, all woods are identical, but their shape and cellular arrangement differs depending on the species. This constitution is equivalent to a diverse physical, mechanical and anisotropic behavior, with an impact on their conservation status. Hence, when pieces of wood in an underwater context are discovered, often the changes occurred make it difficult to identify its species.

To better understand the wood degradation it is important to know about its characteristics and classification as either softwood or hardwood.

When analyzing the structure of softwood (Fig. 7) it shows elongated cells of a uniform diameter (tracheids), which resemble very much thin tubes. Apart from these, in the radial direction arise modular rays, similar to fine and clear lines, which serve to carry and store nutrients. In the transverse direction appear small openings impregnated with oils and resins, called resin channels.

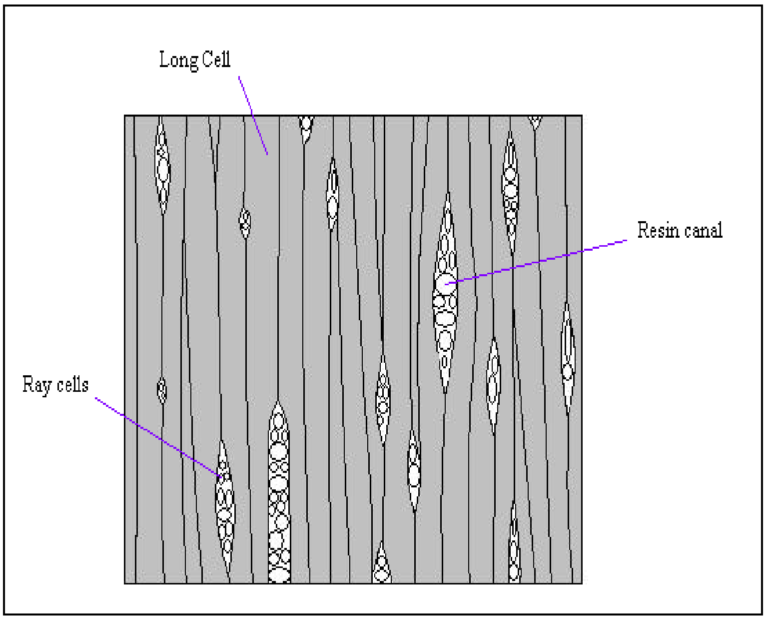

Figure 7 – Long cells of the resinous plants.

For the hardwoods (Fig. 8) their tracheids are considerably smaller, the dimensions across the channels are larger than other elements. Fibers are of a small diameter but a great length, arranged along the stem, forming a very crowded set.

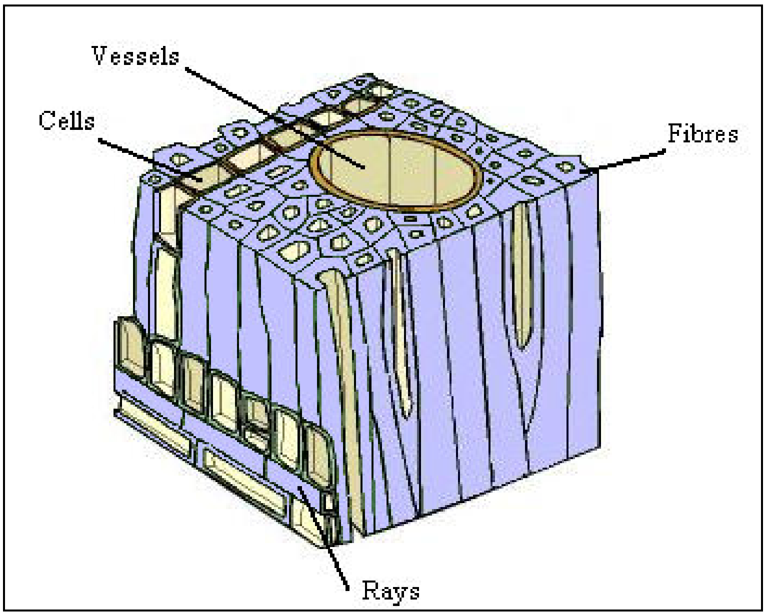

Figure 8 – Schematic disposition of the hardwood tissues.

In particular, and considering the materials found in most underwater archaeological contexts or reported by treatise authors on Portuguese shipbuilding, the Portuguese species that were more used were[115]: the umbrella pine, *Pinus pinea* L.*,* the cork oak, *Quercus suber* L. and the Lusitanian oak, *Quercus faginea* Lam.

In the event of scarcity other alternatives were reportedly explored such as the oak *Quercus ilex* L.; the kermes oak, *Quercus coccifera* L.; the maritime pine, *Pinus pinaster* Ainton; the chestnut mill, *Castanea sativa* Mill; the European silver fir, *Abies alba* Mill; the cedar, *Cedrus sp*.; the cypress, *Cupressus lusitanica* Mill; the Corsican pine and larch pine, both subspecies of *Pinus nigra* Arnold; and the poplar or aspen, *Populus sp.;* including wood imports from northern Europe, especially species of oak, *Quercus sp*..

The environmental preferences of pine makes it possible to be found in areas of sandy soils, like sand dunes near the sea, which allowed its easy transportation to shipyards. Because it is very impermeable, it was believed that this material was resistant to the action of tropical waters, hence its use for hull planking.

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[115] It is not our intention to present a detailed analysis of the works and studies of shipbuilding made in the sixteenth century. For that we simply present the materials used in the work reported in the work of Fernando Oliveira and Lavanha. OLIVEIRA, Fernando - Livro da Fabrica das Naus…; LAVANHA, J. – Livro Primeiro da Architectura Naval…

Another wood quite commonly used in XV and XVI century ship building was oak *Quercus faginea* Lam[116], especially used for frames. Despite being vulnerable to marine borers, its use was favored by shipbuilders due to its density, mechanical strength and aesthetic appearance. In addition, this species grew, at that time, on much of the Iberian Peninsula and also North Africa[117], and was an available resource.

The use of oak was due to its physical properties, in addition to the use of its natural curves, free of knots, making it ideal for building the skeleton of the ship[118]. Despite being considered a high-strength wood it has a tendency to crack. This is due to the substantial differences between the radial and tangential shrinkage, to the high anisotropy, high content of fiber, saturation and hygroscopicity[119].

As mentioned above, other woods could be used, like chestnut wood and kermes oak employed, for example, in the building of the frames. These woods are solid, very hard and compact, and grow all over the country, making them easy to obtain. Despite these characteristics, they were mostly a secondary choice, because they suffer from severe deformation and breakage during drying and are difficult to work with.

Cedar, cypress, pine larch, poplar, and again, chestnut wood were used for planks[120]. Cedar wood, due to its reduced linear shrinkage, volumetric and mechanical properties would also be particularly suitable for internal parts. The use of Corsican pine implied a greater difficulty of operation, especially in sawing. This, along with wood defects would limit its use. Furthermore, this wood is quite susceptible to deformations, xylophagous insects and fungi hindering even more its application. The use of poplar would be limited because it has little flexibility and an average impact resistance.

The *pinus pinaster* Aiton would be reserved for masts and spars but may also have been employed in the upper strake of the hull, above the water line.

Wood import was initially related to the demand of timbers with specific characteristics better suitable for specific ship's timbers, as in the case of Northern Europe where timber imports were used, almost exclusively, for the construction of the masts. At a later stage, the wood shortage in Portugal was such that imported wood was

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[116] About the use of this oak species see CASTRO, Filipe b) – The Arade Ship… p. 55.

[117] On the properties of oak, its location and use see the fundamental work of CARVALHO, A. - Madeiras Portuguesas...

[118] OLIVEIRA, Fernando – *Op. cit.* p. 63.

[119] SOUSA, Vicelina B.; LEAL, S.; PEREIRA, H. - Avaliação de algumas propriedades físicas da madeira de sobreiro (*Quercus suber* L.)…

[120] LOUREIRO, V. - O Padre Fernando Oliveira e o *Liuro da Fabrica das Naos*… p. 355.

ultimately used in large quantities in Portuguese shipbuilding. One of the main imports for shipbuilding purposes was oak from Flanders[121].

Randomly, and judging by the advice of the author of the *Livro Fabrica das Naos*, Fernando Oliveira, in terms of maintenance or repair of vessels in the North Sea, Indian or China, other types of woods could also be used, including exotic wood such as Brazilian wood or teak, provided they resembled those intended to be replaced[122].

13. Environment

Artifacts degradation is a congenital and inevitable process occurring at a variable rate depending on the material's composition and its reaction to the surrounding environment.

Any change occurring by virtue of physical, chemical or biological factors, results in a particular type of pathology, sometimes presenting a specific aesthetic or different visual effect from the original appearance. However, these changes are not always entirely due to a specific process of decay, but rather the combination of several existing ones.

Whatever the degradation mechanism, the environmental conditions play a key role in this intensity value. This is because all materials tend towards a balance with the surrounding environment. When an artifact comes into contact with an underwater environment, the amount of water within that material increases progressively and this absorption will continue until it reaches its saturation point and environmental balance. If a loss of water occurs in the surroundings, the amount of water absorbed will decrease respectively until a new equilibrium value is reached. In this sense it is necessary to study the environment and its effects.

13.1. General characteristics of water

Water is the key element to consider as it has some physical and chemical characteristics, which are extremely important and interesting to highlight. On the

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[121] COSTA, Leonor Freire b) – *Op. cit.* p. 189.

[122] OLIVEIRA, Fernando - *Op. cit.* p. 66.

surface of the Earth, the mass of water is composed of 97.4% salt water and 2.6% of fresh water, making it one of the most common and important substances, the venue for the main biochemical processes of life. This mass is part of the oceans (Atlantic, Arctic, Pacific and Indian Ocean), which represent about 71% of the Earth, with an average depth of 3800m, which can reach 11000 m. It is estimated that the volume of existing water in the oceans is 370 x 106 Km^3.

Chemically, water (H_2O) is a molecule with an extremely stable structure, composed of hydrogen and oxygen in a 2:1 ratio, in which by means of a covalent bond valence electrons are shared. This phenomenon causes an asymmetric distribution of electric charges, resulting in a molecule with a negative charge on one side and a positive charge on the other, forming what is called a dipole. The bipolar nature of water allows its negative side to attract loads of positive nature, while the positive side of the molecule is attracted to negative charges[123].

This element, depending on molecular interaction with the solute, has a broad-spectrum ability to dissolve solids, liquid and gases. The preferred way of solubilization can be distinguished into three groups. The first one interacts with non-ionizable polar substances. In this process, solubilization occurs upon the formation of hydrogen bonds by molecules that contain oxygen or nitrogen, specifically between the groups (OH) and (NH_2) with water molecules to form stable complexes. The second group exploits water bipolar nature, promoting interaction with ionizable substances. In this case, solubility can be achieved via the neutralization of the attraction between electrical charges, forming a very high dielectric constant. Thus, each ion in solution has a special field of electrical insulation which would lower the attraction between opposite electrical charges. Finally, the third solubilization group occurs through non-polar substances. This process is based primarily on the interaction of Van der Waals forces that promote water's contact with compounds, including neutral amino acid molecules, thus promoting its dissolution.

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[123] TAIZ, L.; ZEIGER, E. - Plant Physiology… p. 792.

13.1.1. Luminosity

The presence of light is essential for the production of primary energy for photosynthesis, allowing the creation of all life in the biosphere and the behavior of individuals living in different strata.

The absorption of light by water is influenced by factors such as weather, season, incidence angle, wavelength of light, quality and depth. In rivers, the light penetration is less than in ocean waters. Furthermore, water columns above 30m in depth act as a huge prism, refracting light radiation and filtering the reminiscent wavelengths.

Seawater provides three distinct light zones: a euphotic zone (up to 100 meters deep), which receives higher light, observing in the first meter of depth a strong presence of the red spectrum of radiation, orange and yellow; an disphotic area (between 100 and 300 meters deep), that receives less than 0.0062% of the light that reaches the ocean surface, and an aphotic zone (below 300m depth), with a total absence of light.

13.1.2. Temperature

Another determining agent is temperature. When temperature increases, the levels of dissolved oxygen are affected since its solubility is reduced. Temperature affects the solubility and chemical reactions rates, which occur faster at higher temperatures. The biological process is also affected, since temperature influences metabolism, growth and reproduction, as well as aquatic ecosystem species composition, because many species survive only within a limited temperature range. Finally, temperature has an effect on water density.

Water temperature varies in function of latitude and depth, but depends on two basic variables: solar radiation and water column depth. For example, water temperature shows diurnal variations, which change according to the season. In a river, the temperature will depend upon geographical location plus the river length and stream flow. It may also be affected by the temperature of the inflows, air heat exchanges or acquisition and loss through evaporation or condensation, meaning besides seasonal variations there are also daily differences. Also, temperature variations are higher in fluvial water than in seawater.

As for lakes, temperatures vary with depth according to the lake's characteristics and sunlight depth penetration.

In the case of ocean waters, the effects of radiation and water column distribution are even more evident[124]. Solar radiation near the poles travel obliquely, thereby passing through a higher layer of atmosphere, causing in these ocean surfaces a lower incidence out to the atmosphere (about 40%) compared to the equatorial zone.

On the other hand, temperature in ocean waters varies according to different seasons, but also due to depth, decreasing progressively, with distinct profiles depending on the region of the globe. Thus, in the equatorial region the temperature of ocean water decreases about 20ºC during the first 250 meters of depth, while in regions of high latitudes the difference between surface waters and depth is much smaller.

13.1.3. Dissolved gases

The atmosphere, biological activity and various processes of organic matter decomposition are the main generators of gases that become dissolved in the waters of both rivers and oceans. Two gases: oxygen (O_2) and carbon dioxide (CO_2) are the most significant, either by the quantities or by their importance in many chemical reactions, which are responsible for life in the biosphere.

The amount of dissolved gases depends on the nature of each gas, but also varies with solubility, which is directly related to temperature and altitude. The solubility of gases decreases when the temperature increases, hence, river waters have a higher amount of dissolved oxygen than sea water, since rivers typically have a temperature lower than seawater. With altitude increasing there is a decrease in atmospheric pressure, so oxygen solubility in water decreases and since many rivers originate in higher areas they present a higher oxygen concentration in that area.

The amount of oxygen present in rivers is only substantially reduced with the incorporation of organic matter, which may come from the release of domestic sewage or industrial effluents. This increase of organic matter results in microorganisms' higher

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[124] RILEY, J. P.; CHESTER, R. – Introduction to Marine Chemistry... p. 42-43.

respiration rate, and this gives rise to a major concentration of carbon dioxide and methane (produced by anaerobic degradation) and a reduced oxygen concentration.

The ocean oxygen is introduced by direct contact absorption between the atmosphere and the ocean. At the surface oxygen content is higher, but is substantially reduced after a few meters depth when entering the euphotic zone. This is due mainly to the consumption of this element by the bodies that carry out aerobic processes for energy production, such as plankton, that forms the major part of marine life.

Carbon dioxide, existing in the oceans, comes from the atmosphere but is also formed by sub-products resulting from aerobic processes of energy production by living beings, especially photosynthesis, where its distribution is very similar to that of oxygen. The presence of this molecule causes an acid chemical reaction with the formation of carbonic acid ($CO_2 + H_2O \leftrightarrow H_2CO_3$). As the ocean waters have an alkaline and buffering nature the production of this acid has little influence in the pH.

Due to the oceans' high salt content, the pH ranges between 7.5 and 8.4, so it is predominantly alkaline. In addition to this oscillation, the pH varies along the water column, at the first 50 meters of the euphotic zone it can reach up to values between 7.1 and 7.3. This is due to low concentrations of oxygen (O_2) and very high amounts of carbon dioxide (CO_2), which interact with water to form carbonic acid (H_2CO_3), slightly acidifying the medium.

After this euphotic level, depth increase promotes the pH increase, reaching the final value of 8.4 pH.

Other factors such as salinity, temperature and photosynthesis may also contribute to the oceans' alkalinity.

13.1.4. Reduction Potential – Oxidation/Reduction in Marine Environments

The reduction potential (Eh) quantitatively measured in volts (V), or millivolts (mV) determines the tendency of a chemical species to oxidize (lose electrons) or to reduce (acquire electrons). In other words, it is possible to analyze how the oxidation reaction takes place in an oxygen environment, since oxygen when combined with another element or compound gives out electrons, verifying the opposite in the reduction reactions.

In rivers, the oxidation and reduction reactions are specifically related to the gains and losses of electrons caused by organic compounds, i.e., the oxidation state of elements such as nitrogen (N), sulfur (S) and iron (Fe) present in water, which are also dependent on oxygen presence. That is, the Redox-potential of a river depends on the oxygen level and the amount of organic matter, and therefore may vary greatly. In oceans and seas, the water column is rich in oxygen readily available for ion exchange, as in the section next to the ocean floor there is an anoxic region, providing the absence of chemical reactions with oxygen.

The Redox Potential in the marine environment is identified by four distinct zones: a "zone of oxidation (+700 to +400 millivolts), an area slightly reduced (+400 to +100 millivolts), the other of a moderate reduction (+ 100 to -100 millivolts), and an extreme reduction zone (-300 to -100 millivolts)[125].

13.1.5. Salinity

The water from rivers or lakes is part of the hydrological cycle, which means that it comes from precipitation through a drainage basin area from surface runoff and other sources such as groundwater resources, springs or by the melting of natural ice and snowpacks or glaciers. Because of this, it has no salinity in it, which is why it is usually referred to as freshwater.

As the estuaries are a transition zone between rivers and oceans, they are subject to tides, waves, and the influx of saline water, that comes from sea or ocean; and also flows of fresh water and sediment from the rivers. Characteristics that make this enclosed coastal body of water to be considered as it has medium or low salinity areas.

In the case of seawater, it consists of a set of chemical elements, which give it a specific character, among which ions play the major role (Table 1), contributing to the salinity effect.

The salinity of seawater is given by the relationship between the amounts (gr.) of dissolved salts per kilogram of water, being the benchmark 35% (Table 1).

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[125] FLORIAN, M.- L. E. - The Seabed Environment... p. 15.

Table 1 – General chemical composition of seawater

Category	**Examples**	Concentration rates
Ions		‰ (g/Kg)
Cation (Positive Ions)		
	Na^+	10.6
	Mg^{2+}	1.2
	Ca^{2+}	0.4
	K^+	0.4
	Sr^{2+}	0.01
Anion (Negative Ions)		
	Cl^-	18.9
	SO_4^{2-}	2.6
	HCO_3^-	0.1
	Br^-	0.07
	$H_2BO_3^-$	0.03
	F^-	0.001
Others		0.69
Total		35.00
Gases	N_2, O_2, Ar, CO_2, N_2O, $(CH_3)_2S$, H_2S, H_2, CH_4	nM → mM
Nutrients	NO_3^-, NO_2^-, NH_4^+, PO^{3-}_4, H_4SiO_4	µM
Trace Metals	Ni, Li, Fe, M, Z, P, Cu Co, U, Hg	< 0,05 µM
Dissolvid Organic Compounds	Amino acids, Humic acids	ng/L → mg/L
Colloids	Sea foam, flocs	≤mg/L
Particulate matter	Sand, clay, dead tissue, marine organisms, faeces	µg/L → mg/L

(Adapted from JONES, Mark, ed. - For future generations.., p.14).

This parameter varies between different oceans and seas, but also with the depth of these[126], being dependent on the evolution of temperature. The salinity is also raised by evaporation and reduced by rainfall, river discharge, fresh-water runoff from land and the melting of ice[127].

Salinity levels range between 35-36‰ in the Atlantic Ocean (which affects Portuguese territory), as the Arctic Ocean shows a maximum level at 32‰. Due to the rate of evaporation, landlocked seas show even greater salinity levels, such as 37-40‰

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[126] STEWART, R. H. – Temperature, Salinity and Density... p. 75-104.

[127] RILEY, J. P.; CHESTER, R. – *Op. cit.* p. 44-45.

in the Mediterranean Sea and 40-41‰ in the Red Sea[128]. At higher latitudes, with greater levels of precipitation that exceed evaporation, salinity decreases and the same happens in polar seas during the summer, due to the melting of ice. Since rivers discharge to seas and oceans lower salinity, levels are also found near the coast of continents.

13.1.6. Water density

The density of fresh water is 1kg/l or 1000 kg/m^3, while the seas and oceans have a higher level (1027 kg/m^3), a circumstance which is due to the fact that sea water is richer in salt and therefore denser.

There are two factors that influence the density of ocean water: temperature and salinity[129]. The ocean temperature is the main agent disturbing the density of water, as when it increases it promotes an inversely proportional reaction, thus, the oceanic waters are denser when temperatures are lower. Since the ocean temperature decreases with depth, it implies that the seafloor water density is higher.

Salinity directly promotes the increase of the density of water in oceans and seas: as observed previously the higher the salinity present in water, the denser it will be.

In the case of water with the same salinity, the one that has a higher temperature will float on the one with a lower temperature; this means that temperature promotes circulation in the upper layer of water, even with higher salinity.

The movement of deep ocean water is done through horizontal movement as the less dense water floats on the surface of the oceans and the thicker moves through the bottom, so it moves through layers of the same density. The waters that have the highest density are located in Antarctica and in the Atlantic Ocean, since they present very low temperatures.

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[128] *Idem* p. 56.

[129] RILEY, J. P.; CHESTER, R. – *Op. cit.* p. 29.

13.1.7. Rivers, Estuaries, Lakes and Oceanic currents

River currents depend on many factors such as landscape, topography, soil type, intensity of the rain and watershed of the fluvial system. This system is supported by three major zones[130]: the erosional zone, the transports zone and the depositional zone. The first one is supported by a net erosion of bed material. In the second zone the sediments are transported though the degradation channels. Finally, the last one is formed by the net sedimentation and aggradations channels[131].

In periods of intense rainfall or flooding, sediments may be projected from rivers into the interior of the ocean[132]. The stream flow is also controlled by the force of the tide: when the tide is high the stream flow recedes, when the tide is low the stream flow of a river will undergo a remarkable increase.

The river currents are distinguished according to their origin, such as the descending currents, which flow towards the river, the contrary currents and the undefined currents.

As for estuaries, their currents are determined by the interaction of the geometrical configuration of the estuary, rivers discharge and tidal currents.

In the basic estuary circulation, the fresh water is less dense than the seawater and easily enters through the head of the estuary and flows seaward. The seawater enters in the estuary truth a depth movement and flows up the estuary. As a result of this circulation, the fresh water tends to mix with the seawater producing a range of salinities through the estuary.

According to this process of mixed waters, the estuaries are classified in four types of circulation patterns: i) Salt wedge estuaries; ii) Partially mixed or slightly stratified estuaries; iii) Well mixed or vertically mixed estuaries; iv) Highly stratified or Fjord-type estuaries[133].

In the salt wedge estuary the river flows dominates tidal motion and pushes fresh water out to sea. This cause a low friction of the sea water layer to extend upriver to mean sea level, and promotes the overlying of the denser sea water into the fresh water layer, thus creating water circulation (e.g. Mississippi River, Douro Estuary).

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[130] JULIEN, Pierre Y. - River Mechanics...
[131] *Idem*.
[132] As an example see GARCIA, Carla; [*et al.*] – As plumas turbidas dos rios Tejo e Sado... p. 941-945.
[133] PICKARD, George L.; EMERY, William J. - Descriptive Physical Oceanography…p. 281-284.

The water circulation in the partially mixed estuary is originated by a mixing process of freshwater and saltwater which occurs in all depths, however, the lower layer remains saltier than the upper layer (e.g. San Francisco Bay).

The vertically mixed estuary presents highly mixed water layers and the salinity field is homogeneous from bottom to surface. The salinity values increase horizontally from zero, in the head, to values similar to the surrounding ocean in the mouth of the estuary. This circulation system is created by the eddy diffusion, in which salt diffuses from the mouth, at all depths, towards the river head (e.g. Chesapeake Bay, Guadiana Estuary and Tagus Estuary).

The highly stratified estuary is found mostly in Fjord-type systems and presents a strong vertical salinity gradient. Generally, the upper layer increases in salinity from proximally zero in the river head to a level close to that of the outside sea at the mouth. The deeper layer of the whole basin of the estuary presents a uniform density and the circulation is created by the water movements between the net outflow in the upper layer and inflow in the deeper water.

The lake currents processes are ruled by forces acting in the water body and within the water mass. The mechanisms responsible for generating lake circulation are the river through-flow, wind, heat exchange between water and sediment, and atmospheric heat exchange. These factors are also important for the establishment of the density currents.

Lakes are classified in three major groups according to seasonal patterns[134]: the meromictic, the holomictic and the amictic lakes. The meromictic lakes do not undergo complete circulation of the entire water column: in these case the water mass is permanently stratified and separated in two layers by the salinity gradient not interacting with each other, and these lakes have at least one year cycle.

In the holomictic lakes water circulates, throughout the entire water column and in temperate regions, at least twice annually. The holomictic group is divided into Monomictic (one complete circulation per year), Dimictic (two circulations per year, one in spring and the other in autumn), Oligomictic (few circulation per year) and Polimictic (many circulation per year, normally these lakes have daily circulation).

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[134] LEWIS, William M., Jr. – A revised classification of lakes… p. 1779–1787.

As for the amictic lakes, they are normally located in equatorial regions (high altitudes) and in very high latitudes. They are normally covered in ice, thus, they do not have circulation[135].

Ocean currents are huge movements of water in horizontal and vertical plan influenced by innumerous factors. The oceanic and atmospheric circulations are connected together, and they have the ability to influence world climate. The ocean circulation system is responsible for transfers of heat from low to higher latitudes, and for this reason oceans are responsible for about 40% of global heat transport.

There are two large groups of ocean currents or ocean circulation, the surface currents (surface circulation) and the deep currents (thermohaline circulation)[136].

The surface ocean circulation is induced by three major factors: Global winds, Coriolis effect and Continental deflections[137].

Global winds are strongly influenced by the wind patterns of the atmosphere. The action of prevailing winds creates the large cells of atmospheric circulation, as Hadley cells (predominant in tropical and equatorial latitudes), Ferrel cells (cells of meridional circulation average) and the Polar cell [131], forcing the surface currents to follow the direction of the wind and causing friction between the wind and water, creating waves and the movement of a water column of at least 100m[138].

The Earth´s rotation has a huge influence on the action of the winds and surface currents creating the Coriolis effect, responsible for moving large circular loops of water (gyre). In the northern hemisphere, the Coriolis effect presents clockwise gyre and in the southern hemisphere an anticlockwise gyre. The principal gyres are the North Atlantic Ocean Gyre, South Atlantic Ocean Gyre, North Pacific Ocean Gyre, South Pacific Ocean Gyre and Indian Ocean Gyre[139].

In the Northern Atlantic Ocean, the clockwise rotating gyre consists of the movement of the flowing warm North Equatorial Current from the equator and joining the western boundary of the warm Gulf Stream forming the warm North Atlantic Drift.

The transport of the cold waters from the north is made by the cold Labrador Current, West Greenland Drift, and East Greenland Drift. The closing of the North Atlantic Ocean gyre consists of bringing cold water towards the equator from the closed

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[135] VON SPERLING, Marcos; CHERNICHARO, Carlos Augustos de Lemos - Biological Wastewater… p. 143.

[136] ERNST, Wallace Gary - Earth Systems… p.162-175.

[137] APEL, J.R. - Principles of Ocean Physics… p. 32-36.

[138] ERNST, Wallace Gary - Earth Systems… p.162-175.

[139] MONGILLO, John; ZIERDT-WARSHAW, Linda - Encyclopedia of Environmental Science. p. 256.

connection between the eastern boundary and southward Canary Current to West Africa.

The anticlockwise gyre of the southern part of the Atlantic Ocean is created by joining the South Equatorial Current and Brazil Current, passing the east coast of South America in the direction of Antarctica, where it meets the cold Falkland Current.

The cold waters of the West Wind Drift moving east bypass Antarctica. The cold Benguela Current flows north to the southwestern coast of Africa and closes the gyre. The eastward movement of the warm Equatorial Countercurrent connects the North and South Atlantic Oceans gyres.

In the northern part of the Pacific Ocean, the clockwise rotating gyre originates with the flowing of the warm North Equatorial Current westward, north of the equator, and connecting to the warm Kuroshio Current. Then, it turns to the east and becomes the warm North Pacific Drift. The cold water from the north flows through the cold Oyashio Current and loops in the Alaska with the warm Alaska Current. The California Current integrates the eastern boundary and is responsible for bringing cold water towards the equator, closing the North Atlantic Ocean gyre. In this area there also occurs the upwelling phenomenon[140] which involves a process called divergence, with different natures, consisting of the replacing of the surface water which has moved away with the action of the persistent movement of the sea water to an upward motion towards the ocean surface[141].

In the southern part of the Pacific Ocean, the westward South Equatorial Current (warm current) flows past the east coast of Australia in the direction of the South.

The West Wind Drift flows east approximately to Antarctica and the gyre is closed through the northward movement of the cold Humboldt Current at the southwestern coast of South America.

The Indian Ocean gyre is formed by the warm North Equatorial Current, the South Equatorial Countercurrent, the South Equatorial Current, the eastward and the cold West Wind Drift. This system is influenced by seasonally changing winds (monsoons).

The gyres present different shapes and intensities of flow currents: on the western peripheries of the ocean basins they are intense and asymmetrical (e.g. Gulf

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[140] ERNST, Wallace Gary - Earth Systems… p.162-175.

[141] SANTOS, F.; [*et al.*] – Upwelling... p. 213-218.

Stream, Kuroshio Current), but on the eastern side they are relatively extensive and slow, flowing towards the Ecuador (e.g. Canary current)[142].

Continental deflections also influence ocean currents, dimension and shape of the continent, working like a barrier, forcing water to change the pattern and the intensity of current flow, deflecting the flows of the westerly polewards and the easterly equatorwards, originating closed ocean gyres. An example of this: the continents of Asia and Australia, deflect the currents movement from west in the Pacific[143].

The deep ocean currents or thermohaline ocean circulation results from vertical and meridional overturning circulation at higher latitudes in the northern and southern hemisphere forming a closed loop, called the Great Ocean Conveyor, and are influenced by density gradient, temperature, salinity and ocean surface currents[144]. Conveyor circulation is divided in two parts: one responsible for carrying upper warm ocean waters from tropics and subtropics to the polar regions; the other responsible for the deep transports of cold dense waters from polar regions southward[145].

The Ocean Conveyor begins with the flows of the Gulf Stream and North Atlantic current, transporting saline surface waters from the equatorial Atlantic Ocean into the high-latitude North Atlantic Ocean (near Greenland and Iceland). Here, due to the arctic temperatures, the water is cooled and turns saltier because salt does not freeze when sea ice is formed. For this reason water is denser and downwelling to the ocean bottom, forming the North Atlantic Deep Water. This Deep Water then flows southward along the continental slope of North and South America towards Antarctica.

13.1.7.1. The influence of ocean currents on the Portuguese coast

The Portuguese coast suffered profound changes in the last 18000 years which were influenced by many factors, climate change being one of the most important.

In the Last Glacial Maximum, the North Atlantic Ocean, an important component of the Great Ocean Conveyor, became considerably cooler and the flow was significantly reduced. These phenomena led to the formation of ice in the Continent Shelf and Atlantic Ocean. In Northern Portugal, the Gerês and Estrela mountains were

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[142] ERNST, Wallace Gary - Earth Systems… p.162-175.
[143] APEL, , J.R. - Principles of Ocean Physics… p. 32-36.
[144] FIÚZA, A.F.G. - Introdução à Oceanografia... p. 17-33.
[145] VAN AKEN, Hendrik M. -. The Oceanic Thermohaline Circulation… p. 5-9.

covered by glaciers and the Atlantic Ocean (near to the latitude of Oporto) was covered by icebergs, a situation influenced by the winter coastal water temperature of below 4ºC[146], causing in the shoreline an advance between 120-140m below, compared with present levels[147]. This period was characterized by a combined effect of spring ice melting and high pluviosity levels leading to high fluvial discharge causing a strong sediment supply to the coastal zone.

The last deglaciation (13000 to 11000 years BP), was characterized by the reappearance of the Gulf Stream, affecting the oceanic circulation in the North Atlantic and extensive climate changes with ocean temperature similar to the present. These changes resulted in Western Europe in an enormous decreasing of ice (sea and continental) quantity. The melting ice process led to enormous amounts of the available water, which supplied rivers and produced the transport of small and fine granulometry sediments to the shelf, making the stabilization of the estuaries impossible. The sea level reached to – 40 m below present level[148].

In the Young Dryas (11000 years BP) the climate changed again and became cold with glacial characteristics, with the polar front dislocation to a latitude near Galiza, causing the reduction of the sea level to levels between - 40 to -60m below the present level. In this period, the estuaries become great suppliers of the sediments to the Portuguese Shelf, with extensive accumulation of sand and gravel[149].

When the present level of the sea was reached (between 3000 and 5000 years BP) the littoral shape was substantially different from today: the coastal littoral was essentially rocky, with intensely and irregularly incised and open estuaries.

Today, with the increasing of the sea level the terminal areas of the lagoons and estuaries are overflowing with sediments, and in some cases it is possible to verify the formation of delta structure in the estuaries (e.g. marshlands of the Tagus River). This amount of sea water leads to a strong and quick erosion process of the coast line promoting the erosion of the sandy coastal line (e.g. Algarve).

With the increase in the sea level the Portuguese Margin is influenced by the regime of strong winds related to the migration of the subtropical front and the effects of the Azores anticyclone cells. This anticyclone is responsible in the winter for the westerly winds off the Atlantic Iberian coast, and in the summer by the strong northerly

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[146] DIAS, J.M.; [*et al.*] - Coast line evolution in Portugal…
[147] DIAS, J.M. Alveirinho - A história da evolução do litoral português…
[148] DIAS, J.M.; [*et al.*] - Coast line evolution in Portugal…
[149] DIAS, J.M. Alveirinho - A história da evolução do litoral português…

and northwesterly winds, inducing the Ekman transport offshore along the western coast[150], causing a seasonal coastal upwelling from July to September[151]. The coastal upwelling results from the combined action of three agents[152]: i) regime of the wind blowing; ii) the Coriolis effect and iii) the presence of a solid boundary (e.g. coasts).

On the western coast, the upwelled water flows southeastward and eastward, but with the influence of the west winds from the Gulf of Cádiz, the upwelled waters flows east through the southern coast. Close to Faro, it is possible to observe a small upwelling area into the east of Cape Santa Maria[153].

13.1.8. Oceanic Physiographic

The bottom of the deep ocean is characterized by the existence of an enormous diversity of materials, which are deposited in the form of sediment, and may have various origins and sizes.

With regard to their origin they are classified as: i) Lithogenic sediments (such as silicate grains) which result from the degradation of continental rocks or volcanic activity; ii) Biogenic sediments, from deposits of insoluble residues of bone, whale teeth and shells of marine organisms; iii) Autogenic sediment, derived from the chemical reactions of the marine environment (evaporites, carbonates or polymetallic nodules); iv) Cosmogenic sediments, which have a cosmic origin or cosmogenic, consisting mainly of particles from the cosmos[154] with dimensions between 10 to 1500m[155] (Alveirinho). These are responsible for particles such as: i) Silicate chondrules, which have in their composition minerals such as augite (ferro-magnesian mineral), olivine (ferromagnesian mineral) and pyroxene (the most common ferromagnesian minerals); ii) Iron spherules, highly rich in elements such as iron and nickel with diameters which can reach 30m; iii) Micro-Tectites, which are glassy (highly rich in silica), round or teardrop-shaped particles with dimension between 0.03 to 1.5 mm in diameter; and iv)

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[150] SOARES, António Monge; Dias, João. M. Alveirinho - Coastal Upwelling and Radiocarbon… p 45–60.

[151] SOARES, António Manuel Monge - Variabilidade do “Upwelling” Costeiro… p. 1-28.

[152] SANTOS, F.; [*et al.*] – Upwelling... p. 213-218.

[153] VARGAS, J.M.; [*et al.*] - Seasonal and wind-induced variability…

[154] The origins of oceans and oceanography concepts can be seen in BROWN, Geoff .C.; HAWKESWORTH, C.J.; WILSON, R.C.L. eds. - Understanding Earth. …

[155] DIAS, J. Alveirinho - A Análise sedimentar…

Tectites, glass bodies with black to green colors, normally associated with microtectites [156] with a diameter between 2 to 4 cm.

Another important factor in the characterization of existing sediments on the ocean floor is the classification according to size from which it is possible to see the mode of transport and distance from the point of origin to the site of deposition. That is, the existence of a large proportion of sediment with uniform size, assumes that in this process it a high level of mechanical energy environment was involved, such as the beach sand when being dragged to the seafloor.

13.1.8.1.Physiographic types of seafloor

The ocean is divided into three major physiographic provinces[157]: continental margins, ocean basins, and oceanic ridges.

Continental margins are the extension of the continent by direct contact with the ocean, that is, the zone that separates the sunken continent of an abyssal plain or deep ocean. Being constituted by the continental crust (part of the continent which is under the direct action of the sea and is defined by the area between high tide and low tide), the continental shelf (surface underwater, in the continuity of the coast, with a slope reduced by 5 and a depth of 200m about 0-350 km from the coast), the continental rise (large gradient zone in which the depth of 100-200m decreases to 1500m depth, ranging between 350-390 km from the coast, occurs in places where a continental block bordering an abysmal pit) and continental slope (transition region between the continental slope and the deep ocean, with a depth of 1500-4500m, and can reach greater depths, extends between 390-860 km from the coast, presents a relief fund, except for the areas where submarine canyons extend their channels to the massive submarine)[158].

The ocean basins or deep ocean floor cover about 29.5% of the earth's surface[159]. The topography of these floors is formed by volcanic activity and tectonic processes, containing the abyssal plains (large flat areas located around the border ocean of the

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[156] *Idem*.

[157] The aspects of the ocean physiography are very well present in the work of TESSLER, M. G.; MAHIQUES, M. M. de. - Processos oceânicos... p. 262-284.

[158] KENNETT, J.P. - 1982 - Marine Geology. Prentice-Hall Inc. Englewood Cliffs, N.J., 435 p.

[159] We can find an analysis of the ocean basins in FIÚZA, A. – *Op. cit*. p. 40-46.

continental crust to a depth of 3000-5000m); seamounts (which can be considered as a single unit with a relief of big dimensions, generally, conical which are usually extinct volcanoes that rise over 1000m above the seafloor, forming islands and island arcs, especially in the Pacific); oceanic trenches (depressions or narrow areas with depths that reach 11 km, the greatest depths of the ocean basins); guyots or tablemounts (isolated seamounts truncated by the erosive action of waves below the surface of the sea level); and submarine ridges (forming an elongated elevation of the ocean floor, with a wide range of more marked relief, which includes slopes or cliffs that extend throughout the oceans constituting the longest mountain on earth. These submarine ridges are also associated with an intense seismic activity where fractures and/or rifts can be found[160]).

13.2. Biological agents and degradation

Rivers, seas, lakes and oceans have distinct characteristics of temperature, oxygen, salinity, nutrients, sediment and density. These are the factors that allow the formation of different habitats which, in turn, will foster several interactions with the existing underwater archaeological materials.

It is because of this direct cause/effect relationship that it is necessary to understand the outside environmental changes, plus changes in the internal structure in order to know what can be found in an underwater context, the possible state of conservation, and also provide a conservation treatment, allowing the degradation process to be considerably slowed down.

The underwater environments are the ones that most lead to and promote biodegradation. In a situation of total submersion of the materials, the most common organisms that interact or promote deterioration are bacteria, fungi, crustaceans and mollusks.

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[160] TESSLER, M. G.; MAHIQUES, M. M. de - *Op. cit.* p. 262-266.

13.2.1. Bacteria

Bacteria are part of the natural composition of biomass, and can be found both in aerobic or anoxic environments. The microbial attack receives the name from the environment it comes from: aerobic bacteria or anaerobic bacteria. Apart from these, there are facultative bacteria, which are capable of living in environments with different concentrations of oxygen. This feature gives them a great capacity to adapt to adverse situations, promoting a major colonizing ability in various habitats, mainly by metabolizing organic compounds in order to produce the biomass, needed for their development.

In an underwater context and despite the aerobic degradation process occurring on a smaller scale, it appears that these bacteria are the first to act on the surface of existing sediments on the ocean floor, greatly reducing their action when the depth exceeds 100m. After this level, which corresponds to an anoxic environment, where the nature of sediment does not make the existence of oxygen possible, only the anaerobic bacteria dominate.

Depending on the type of bacteria, various byproducts are generated, so aerobic bacteria produce byproducts such as NH_3, NO_3^-, NO_2^- and CO_2. In the case of anaerobic bacteria, the byproducts are organic acids such as N_2, CO_2 and H_2S. In archaeological woods from aquatic environments besides nitrogen based compounds, phosphorus is also found in bacterial attack[161].

The decay process through bacteria action depends on the micro-environment (water temperature, oxygen availability, salinity and existence of organic compounds), and although they are quite resistant to extreme environmental conditions, not all resist a high moisture content, or complete water saturation and reduced oxygen levels; it also depends on the chemical constitution of the artifacts. Due to these features it is believed that "bacteria are a major factor in the decay processes" [162] as well as the first to attack, especially cellulosic materials[163].

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[161] Archaeological wood and wood from foundation piles decayed by bacteria were chemically analyzed. Besides the differences found in the wood components of each wood, it was possible to identify several chemical compounds, see GELBRICH, J.; MAI, C.; MILITZ, H. - Chemical changes in wood degraded by bacteria... p. 27–29.

[162] KIM, Y. S.; SINGH, Adya P. – Micromorphological characteristics of wood biodegradation... p. 136.

[163] *Idem.*

The microbial attack degrades organic materials by breaking them down or transforming structural components, resulting in the lost of density and mechanical strength.

13.2.2. Fungal attack

Fungi have a great metabolic versatility, a characteristic that allows them to use a huge variety of organic substrates for growth, including extreme environments such as deep water, high concentrations of salts, acidity of the medium, lack of brightness, or high UV radiation, the only constraint to their development being the need for water and oxygen[164].

Among this type of microorganism, those which are developed in underwater environments are called marine, like heterotrophic organisms, or use organic compounds for energy production.

At the morphological level they are composed of a thallus (vegetative body), hyphae (filaments that can be modified to produce highly specialized structures in order to maximize interaction with the substrate available) and mycelium, forming a microscopic network that embraces the material to degrade[165].

Depending on the effects on the material, it is possible to classify the action of these microorganisms into coloration or destructive fungi. The first ones, as they only use nutrients from non-structural components to produce energy without affecting the mechanical properties of materials, just cause a superficial color transformation, turning the surface to "shades of blue, brown, green, or red, depending on the type of organism and substrate"[166].

The second group, which is prevalent in cellulosic materials, includes various groups of fungi, such as: brown, white and soft rot. They act through enzymatic action promoting the degradation of the structure of lignin and polysaccharide components of the wood, turning them into sugars. This attack causes loss of mechanical strength of the cell wall and, ultimately, its utter destruction[167].

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[164] AHEARN, D. G.; CROW, S. A. – Fungi and Hydrocarbons... p.12-13.

[165] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke – Conservation of Wood Artifacts… p. 91-92.

[166] BLANCHETTE, Robert A.; [*et al.*] - Biological Degradation of Wood… p. 142.

[167] *Idem*, p. 141-174.

The rate of degradation varies according to the fungi species and the nature of the elements altered or removed from the artifact.

13.2.3. Marine Borers

Other marine organisms, belonging to a remarkably diverse group which can be found in aquatic environments, are mollusks and crustaceans. Both are particularly harmful to cellulosic materials, especially for wood, because regardless of the nature or degree of hardness of it, they are able to open tunnels or galleries, with vertical or horizontal placement, completely destroying the existing structures.

Mollusks are the most destructive as they are able to burrow deeply and quickly into all kinds of wood, destroying all of its structure. The two most important families of mollusks are the *Teredinidae,* which penetrates and form hard plates of calcareous materials, restricted to 200m depth. It grows in coastal water, warm and temperate zones, as long as the "salt content is in the range of 0.9% to 3.5%"[168]; and the *Pholadidae*, found up to 2000m depth in warm and tropical waters.

Concerning crustaceans, there are two main groups responsible for most damage in wood in underwater archaeological context, the Isopoda and the Amphipoda. Due to the ability to tolerate different levels of salinity and live and develop in cold, temperate and tropical waters, isopods are spread worldwide, and they are also much more destructive than the rest.

14. Organic materials degradation

The degradation of the materials may have several aspects or decomposition rate: sometimes the organic material of underwater environments is presented in its original form, but internally it can contain an altered chemical constitution. There are also situations in which the archaeological elements of organic nature are just a mass, hardly identifiable as to its nature. Contributing factors for this condition are: the chemical constitution, the use and type of artifact and environmental conditions. That is,

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[168] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke – *Op. cit.* p. 135.

to each context and each material correspond a type of degradation and to this one, or several, pathologies that when analyzed allow the identification of the causes and the state of preservation.

In terms of causes of degradation there are three processes: physical, chemical and biological. However, despite this difference this does not mean that they perform in a single way, but rather that one of them can give rise to another type of degradation.

The physical processes involve the deterioration of the properties through erosion or abrasion, promoting the abrasion of the surface, or forces and stresses applied to the material, causing it to stretch or to shrink, with consequent changes in the dimensions and in the molecular structure.

Chemical degradation involves reactions between the original material and the existing elements in the environment. They are the oxygen, water, temperature, radiation, pH, salinity or any other chemical substance. The reactions triggered by these compounds are mainly based on hydrolysis[169] and oxidation. In the first situation by virtue of the water, is the replacement of a component by another molecule of hydrogen (H^+) or hydroxide (OH^-). This operation will cause the appearance of new substances and break the existing links. However, the sole and exclusive hydrolysis by water cannot perform a complete degradation of the structure. In most cases the presence of high temperatures and pressures are necessary, or failing this, the presence of acids, alkalis and enzymes, giving rise to acid hydrolysis, alkaline hydrolysis or enzymatic hydrolysis.

Oxidation is related to changes involving the loss of electrons, increasing the positive valence of a chemical compound. The transformations by oxidation are often caused by radiation, both visible and ultraviolet, as the pollutants in the atmosphere and the aquatic environment.

In terms of temperature, this can be a key element for hydrolysis and oxidation, as when energy is introduced, this increases the activity and molecular collision between molecules occurs. This reaction becomes so severe that the bonds holding the chains fail to resist the movement and they break, causing the dryness and breakage of material, by degrading it. On the other hand, an increase in temperature causes changes in the balance of the environment making it more acidic, because with the rising

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[169] Also called depolymerization or hydrolytic disruption.

temperature occurs the increase of the concentration of hydrogen ions (H^+) and consequently decreasing the pH.

The integrity and stability of the materials depend on the pH. This will influence the chemical reactions since "either a high or a low pH can speed up the hydrolysis of organic materials"[170] or induce oxidation and reduction reactions. Furthermore, pH influences biological degradation, whereas some bacteria are able to develop in pH extremes.

Chemical reactions can also be triggered by the type and quantity of salts existing in the surrounding water. Due to their ability to dissolve, salts penetrate organic material, occupying the interstices of internal structures. Depending on the nature of the salt[171], they can be connected to the matrix or the cell wall in which they accumulate gradually, compressing those regions to the point of damaging the original structure. Salinity is also responsible for osmotic pressure on the materials and also by the conductivity, being directly related to the possibility of occurrence of oxidation-reduction reactions. Finally, salt concentration will determine the type of biological degradation, due to its direct relationship with the diversity and abundance of the community of *phytobenthos*, *zoobenthos* and *protozoa*.

Degradation biological processes are caused by the attack of microorganisms or marine animals. The first group, with synthetic chemical processes, cause the loss of part, or all of the material and results in new organic molecules, whose by-products lead to chemical changes as patches, erosion (by means of acids or enzymes produced) or distortions. The second is primarily responsible for physical abrasion, cracks or gaps.

Finally, it is also important to understand the proximity of other elements that will influence the state of conservation of materials, both for their direct action as by-products released into the medium.

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[170] CRONYN, J. M. - *Op. cit.* p. 20.

[171] A salt the result of a chemical reaction that occurs between three types of elements: a base and an acid; an acid and a metal; or an acid and an oxide acid or a basic oxide.

14.1. Leather, skin, bone and ivory

As stated before, collagen has a very complex structure which composes connective tissue, and the degradation of this material is generally called diagenesis, meaning the changes occurred in collagen and its inorganic components.

The preservation state of waterlogged leather is first related to the products of reactions between ferrous ions and tannins and second due to the burial conditions, both explaining the black or paler brown colors. It is also necessary to consider the content of sulfur compounds or metals, remaining from their manufacturing, because in conjunction with other elements they tend to form harmful compounds, such as sulfuric acid, accelerating its degradation. If the tannins used are not of vegetable origin a better conservation is possible, because they absorb less oxygen and sulfur dioxide from the environment.

There are also external factors that contribute to their degradation, the bigger contributor to the occurrence of chemical changes at the cellular level are hydrolysis and oxidation.

Hydrolysis appears in extreme cases of hydration with a consequent expansion of the fibers and this happens in such a way that the helical chain disintegrates, resulting in the total dissolution of the protein, becoming a sort of gel. In this situation, the level of degradation can be such that the existing chains can no longer be reconstructed.

In the case of oxidation, changes occur at the molecular level, resulting in the loss of mechanical strength, cracks, breakage, adulteration of the solubility of the polymer, changes in pH and variation in color.

For these phenomena to arise, environmental conditions such as extreme levels of pH, salt concentration, temperature, water, oxygen level, presence of metals, gases and ultraviolet radiation must exist.

If water pH is less than 4 or greater than 8, there is an increased concentration of H^+ ions, or increases in the concentration of OH^-, respectively. Given this background and to satisfy the Osmotic Gradient, i.e., to balance the difference in the material, a greater percentage of water penetrates into the collagen, causing the dilation of materials. From this reaction comes an increase in thickness and a decrease in the length of the protein. Nevertheless, it is a situation that can be corrected if force is applied to the material or if the pH is corrected. However, if the presence of an acid pH is constant, irreversible changes, like material darkening, will occur, because acidity will induce chemical changes in the vegetable tannins used in tanning.

The expansion of the fibers can also happen if the level of salinity of the medium exceeds 0.5 M, in this situation salts penetrate and fill the spaces in the polypeptide chain, if there is an evaporation of water, the concentration of salts increases as well as its volume, causing distention of the entire protein structure. This effect will depend on the nature of the existing salts because different salts have different levels of absorption.

The degradation of collagen may also occur due to higher temperatures. The increase of temperature leads to a greater molecular motion which causes the collision of molecules and breaks the triple helix bonds, causing protein denaturation, resulting in a sudden contraction of the fibers and their rupture. In practical terms the material becomes hard and brittle. However, this pathology by virtue of water presence cannot be easily identifiable. The degradation of the fibrous structure causes a significant increase in permeability, so the hide or skin quickly absorb water or other hygroscopic products, which will be located at the fibrils surface, pushing the polymers and increasing their mobility, therefore, the same material may present, throughout its structure, different types of stiffness.

In extreme cases, the combined effect of increased temperature and the presence of water can lead to protein denaturation, with its transformation into gelatin[172]. This gelatin arises due to a partial hydrolysis of collagen. In this situation the initial structure of the amino acids does not degrade but suffers a rearrangement of molecular bonds between the fibers, inducing color and texture changing.

Furthermore, the effect of water on collagen is also related to waters' ability to promote chemical reactions. Water can either act as a solvent in the reactions, leading to an increase in elements concentration, boosting the reaction of chemical compounds percentage, or promoting free radicals formation[173]. In functional terms, by the reaction of the radicals, it is possible to have the appearance of a gelatinous substance or a stiff substance. Free radicals caused either by solar radiation[174] or pollution carry high

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[172] According to ALGER a gelatin is a “partially denatured collagen, in which the intermolecular hydrogen bonds between the individual chains of the tropocollagen molecules have been destroyed”. ALGER, Mark S. M. – Polymer Science Dictionary... p. 217.

[173] Free radicals are molecules highly instable due to their single unpaired number of electrons, which makes them chemically reactive.

[174] The alteration effects of solar and artificial UV radiation upon collagen have already been exhaustively studied and compared. The results are presented in the work of SIONKOWSKA, Alina; [*et al.*] – Effects of solar radiation on collagen...

energy levels and when they come into contact with collagen this energy causes rupture between molecules, resulting in an alteration of their properties.

The UV rays due to a strong wavelength (around 400 nm) are able to promote situations of degradation, as the case of photolysis[175] or photo-oxidation[176]. These lead to: the breaking of carbon bonds present in polymers, transforming them into monomers, so the weakening occurs with a consequent rupture of the material; and also to the loss of mechanical strength, cracking, breaking, alteration of solubility, changes in pH, and color changes all due to modification of the connections and the appearance of new groups and products.

In an underwater context these changes become even more severe. With photo-oxidation energy absorbed by collagen reacts with oxygen to form a free radical which, in the presence of water, forms peroxide, an oxidizing agent[177]. This in turn will lead to an action in the chain until the complete degradation of the material. Since the chemicals used in tanning or in lubrication react to oxidation to form new molecular bonds, the new free radicals derived from oxidizing agents strike the new molecules and form new radicals. That is, the free radicals formed will connect and form new compounds and so on, until the final decomposition of the protein.

Regarding pollution, the most harmful elements are ozone, sulfur dioxide, or nitrogen dioxide. They act similarly to the above-mentioned process, since the presence of oxygen or water molecules react rapidly with organic materials, that is, they are all oxidizing agents, therefore, able to start the autoxidation of elements, leading to the breakup of the polymer chain[178].

Also transition metals are able to promote this type of autoxidation, since they participate in oxidation-reduction reactions that lead to the cleaving of links of collagen. On the other hand, the fact that they are oxidizing agents makes them capable of promoting the occurrence of free radicals which bind to hydrogen in the chain and generate a new radical causing an ongoing peroxidation reaction until final degradation. These are the main phenomena of collagen degradation when combined with metallic elements; however, there are many other specific situations of oxidation and/or hydrolysis that correspond to a specific metal and a specific environmental condition.

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[175] Photolysis is the dissociation of organic molecules by electromagnetic radiation.

[176] Photo-oxidation is an oxidation reaction (loss of electrons) that occurs through the absorption of UV and visible light.

[177] This reaction is also called peroxidation.

[178] About the damaging effects of pollution see THOMSON, Garry – The Museum Environment… p. 130-156.

For these reasons, it appears that despite different reaction mechanisms being involved, hydrolysis and oxidation are related, and both processes act simultaneously or often end up reinforcing each other. Waterlogged leather usually presents a gelatin look and touch, dark to black color, lack of resilience or stiffness[179], delaminating into two separate layers, flaking, fragmentation of the surface, and "weakness of the collagen fiber"[180]. Also iron salts and concretions may disfigure surfaces, hiding the form and nature of objects.

Although they are structurally different materials, bones, dentine or ivory, have a similar composition, so minor differences arise with respect to their deterioration. Nevertheless, despite the inequality, the process of diagenesis[181] is identical to all of them and occurs through dissolution and deposition of other materials.

In terms of dissolution three types can occur: "chemical deterioration of the organic phase; chemical deterioration of the mineral phase; and (micro) biological attack of the composite"[182]. The first is related to dissolution of collagen, connected with the temperature, pH, presence of metals and salinity. In this case, changes give rise to a material with soft, pale characteristics.

Dissolution of minerals concerns the loss of hydroxyapatite, as since this element is quite stable the transformation depends on the acidity of the medium, which promotes the appearance of cracks, flaking or disintegration[183].

Biological attack is the most common form of degradation. It occurs in environments in which are found fungi, bacteria and cyanobacteria[184]. These organisms cause the loss of collagen and increase in porosity, with a consequent increase of the degradation rate, since the gaps encourage further weakening of the material and its disintegration[185].

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[179] An analysis of the conservation state of different types of leather have been discussed and tested, for a better understanding see SOEST, H. A. B.; STAMBOLOV, T.; HALLEBEEK, P. B. - Conservation of Leather... p. 21-31.

[180] CAMERON, E; SPRIGGS, J.; WILLS, B. – The conservation of archaeological leather... p. 245.

[181] Diagenesis is all chemical and physical changes experienced by this type of element from the first moment of its deposition at the time of its discovery. For a general view of chemical diagenesis see NIELSEN-MARS, Christina; [et al.] – The Chemical Degradation of Bone. p. 439-450.

[182] COLLINS, M. J.; [et al.] - The survival of organic matter in bone: a review... p.383.

[183] Information on the details of changes in these materials due to marine burial are available on FLORIAN, M.-L. E. a) – *Op. cit.*

[184] Cyanobacteria are also designated as cyanophytes or blue-green algae (name given because of its greenish blue or green). These bacteria are unicellular aquatic organisms, colonial or filamentous photosynthetic found in continental waters, wet soils or in a hypersaline lakes.

[185] JANS, M. M. E.; [*et al.*] – Characterization of microbial attack on archaeological bone... p.88.

The same applies to deposition of other elements such as the inclusion of exogenous materials which only happens if bone, tooth or ivory present open spaces or gaps. These additions or infiltrations appear embedded in the matrix, producing changes in its crystallinity[186] increasing the degradation rate.

It can also occur the appearance of spots, both in the matrix, or at the surface of materials, and these are related to the diffusion of corrosion products of metal in the underwater archaeological context and its deposition in organic material[187].

In addition to these pathologies, it is possible to have the rising of cracks or breaks: however, these are related to physical conditions and the anisotropic structure of the material and not with chemical or biological events, especially if they have a visible size to the naked eye, or geometrical sections for the ivories.

Each of these changes can cause the appearance of another: for example, the dissolution of minerals in the bone will expose collagen to chemical degradation, followed by an enzymatic attack, with the consequent exposure of the organic material to micro-organisms[188].

14.2. Wool, horn, feathers and tortoiseshell

Keratin is relatively resistant to degradation when compared with other elements, with a greater chance for surviving in extreme conditions, as is the case of the underwater environment. The key to survival lies in the nature of its disulphite covalent bonds, which are not easily hydrolyzed. Keratin hydrolysis occurs only if this protein is subject to a high pH environment. In this situation the disulfide bonds are destroyed and proteins are converted into singular amino acids[189].

By virtue of its chemical composition, it is also resistant to temperature changes, however, in case of temperatures above 100°C "heating breaks down some of the bonds between the protein"[190], causing irreversible deformation of the structure and its consequent degradation.

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[186] GODFREY, I.; [*et al.*] b) - The Analysis of Ivory…

[187] *Idem.*

[188] COLLINS, M. J.; [*et al.*] - *Op. cit.* p.386.

[189] CRONYN, J. M. - *Op. cit.* p. 282.

[190] GOFFER, Zvi – Archaeological Chemistry... p. 384.

In terms of microbial degradation, it is not afected by common proteolytic enzymes, but only by specific enzymes, the keratinases. These enzymes come from keratinophilic fungi and dermatophytes, organisms that colonize the keratinous tissues and are capable of hydrolyzing proteins leading to loss of integrity between the peptide bonds. Considering that keratinase only occurs under extreme conditions of temperature, anoxia or inhibition of metals, this form of degradation can only be expected in exceptional circumstances.

Despite the strength of this protein it is, however, subject to chemical changes caused by radiation, since photochemical degradation triggers hydrolysis and the consequent breaking of disulfide bonds[191].

These materials can be found in a relatively good state of preservation, but diagenesis is to be considered as well as burial conditions. In waterlogged environments the most common form of degradation of keratin materials is due to physical stress, fostered by the weight of deposits that these elements are subject to, forcing its distention and causing its deformation. Also, if subjected to drying out they tend to delaminate or to suffer dimensional changes.

14.3. Hydrolysis and oxidation of silk

When degraded, silk presents a yellow and brittle shade; this state arises by virtue of hydrolysis and/or oxidation of the material caused by chemical factors, which come from agents such as temperature, pH, and radiation.

Despite being water insoluble in the presence of water, silk fibers swell differently according to the direction of each fiber, degrading the fibroin.

Due to its crystalline nature fibroin is highly resistant to chemical attack, but in the presence of a concentrated acid this protein will hydrolyze. The concentrated acids attack the amorphous region, whose peptide bonds are more sensitive, rapidly dissolving it. From this comes a change in hydrogen bonds, causing the interruption of the polymer chain. As a result of acid hydrolysis, silk becomes mechanically weak and brittle[192].

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[191] *Idem*, p.358- 359.

[192] TIMAR-BALAZSY, Agnes; EASTOP, Dinah – *Op. cit…* p. 46-47.

A basic pH environment also deteriorates silk causing depolymerization of fibroin and, with this, the mechanical strength loss and predisposition to other types of degradation, such as the formation of new groups which will transform the fiber in a less flexible and fragile material[193].

Some amino acid residues such as tyrosine, phenylalanine and tryptophan, absorb UV radiation, which causes oxidation of amino acids as well as the rupture of hydrogen bonds and peptide groups, leading to the breakup of the polymer chains, therefore the loss of physical properties. Harmful effects of radiation are even greater in extreme conditions of pH (pH = 3, pH = 11) or if the pH is between 6 and 8. This results in a loss of wholeness, resulting in a weakened and yellowish material.

Sometimes, during the manufacture of silk are incorporated metal salts of iron, lead or tin, which when in contact with a saline environment will act as galvanic cells, making possible the oxidation-reduction reactions and the degradation of woven structures.

Another form of degradation of the fibroin arises after the dissolution of sericin in water, making it very susceptible to attack by microorganisms[194].

Finally, mechanical properties of fibroin suffer significant changes with high temperatures, causing dryness and oxidation of fibers[195]. Dryness is due to the loss of flexibility[196], since water of constitution is removed disrupting the molecules. As for the oxidation it is the result of free radicals thermal oxidation upon amino acid residues, breaking the hydrogen bonds available and causing the degradation of fibers[197].

For these reasons, although theoretically fibroin is a resistant material, in practice in underwater archaeological contexts it is not a very common material because fibers sensitivity makes them very susceptible to degradation.

14.4. Waterlogged wood deterioration

Waterlogged wood is defined as a material that contains no air in its cellular spaces, because all the capillaries and micro-capillaries are water-filled. Its degradation

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[193] *Idem.*

[194] GARSIDE, Paul; WYETH, Paul – *Op. cit.* p. 82.

[195] TIMÁR-BALÁZSY, Ágnes; EASTOP, Dinab - Chemical Principles of Textile Conservation… p. 46.

[196] GARSIDE, Paul; WYETH, Paul – Textiles... p. 80.

[197] *Idem.*

is a complex process and it depends on the relationship and the ratio between the components and the bond of these with the products formed by the deterioration phenomena. Thus, in the same underwater archaeological context can be various decay states for different wooden materials, but also different behavior between the same types of materials.

Like other organic materials, wood degradation process involves physical, chemical and biological factors, which tend to be related to each other. Physical factors cover the deterioration of the properties by stress, loads or other physical factors to which the materials were or are subject to: for example, the collapse during a shipwreck, with the impact on its deposition on the bottom or the strength of tides. These phenomena will lead to changes in terms of dimensions, with the visible appearance of breaks, cracks, abrasions, omissions, distortions, stress of the molecular structure, with changes in the cellular matrix.

Physical phenomenon result also in several chemical changes, and one of them is the swelling of the structure promoted by water penetration. Although water allows materials to remain in a fair condition, it is also considered as an agent of destruction. In general, it is the water content of wood which gives it softness and malleability and the greater the amount of water, the softer it becomes.

If the quantity of water in waterlogged wood is above the fiber saturation point (FSP) it corresponds to the saturation of the cell walls, given by the moisture content of wood (MC), which gives the degree of deterioration of the wood materials. It can be defined as the weight of water in wood given as a percentage of oven-dry weight of wood, according to the equation[198]:

$$\%\ \text{Water} = \frac{\text{weight of wet wood - weight of oven-dried wood}}{\text{weight of oven-dried wood x 100}}$$

Thus, swelling occurs because the water penetrates into the fibrils and microfibrils, through the capillaries and holes, where it is absorbed by the amorphous regions. In those regions water forms hydrogen bonds with the polar terminal groups, such as hydroxyl (OH), allowing water to continue inside the cell wall. While this happens in the amorphous regions, in the crystalline areas where water cannot enter and

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[198] HAMILTON, Donny L. a) - Basic Methods of Conserving ... p. 26.

create bonds, only adsorption takes place[199]. As water continues to enter the matrix hydrates, forcing cell wall polymers apart, then more water moves deeper into the structure and swelling occurs, increasing the adsorption. This will increase fibers flexibility affecting “not only the rigidity of the fibers but also the local plasticity to the cell wall”[200]. Swelling continues until the cell reaches the equilibrium with the ambient humidity or until FSP is reached.

The contents of lignin, hemicelluloses and cellulose differ from one material to the other, which causes variation in the cell walls permeability to water and directly influences decay pattern in submerged artifacts.

This aggregation ability with water is what also allows chemical bonds between fibers and salt solutions, or between fibers and acids or alkalis. That is, the chemical process of degradation is also stipulated by the accessibility of chemical solutions to the cell wall's constituents.

An underwater environment is always an electrolyte (salt solution) where hydrated ions are available to penetrate and connect with cellulosic materials. The bonding that occurs between them is usually very strong and stable, causing different degrees of swelling, changing morphologically the polymers or just dissolving degraded cellulose. Besides, “many inorganic salts in aqueous solutions will dissociate and make the solution more or less acidic or alkaline” [201], which will have effects in terms of degradation actions such as hydrolysis.

The introduction of chemical compounds promotes hydrolysis and oxidation phenomena, which occur at various levels of cellular organization. Since hemicelluloses and cellulose quickly establish chemical links they are the most susceptible to chemical attack[202].

Hydrolysis results in a decrease of polymerization of the cellulose and hemicelluloses, by reducing the size of the polymer chains so their strength and elasticity suffer an alteration. When hydrolysis occurs in an acid medium, the links are attacked causing solubility of polysaccharides, glucose and acidic components. In the case of acidic components this increases acidity and new groups are also attacked. The

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[199] MCCAWLEY, J. C. – Waterlogged Artifacts... p. 17- 18.

[200] HAMAD, Wadood Y. – Cellulosic Materials... p. 64.

[201] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke – *Op. cit.* p. 44-45.

[202] About the degradation of these elements under acidic, alkaline and oxidative conditions see YUAN-ZONG Lai – Chemical degradation... p. 443-512.

prolonged contact with acids results in a brown surface, particularly visible[203]. If the attack is made by alkalis then the material degraded is lignin, and wood will appear as "fibrous character (…) with certain white rots"[204].

Hydrolysis can also cause chemical changes by the swelling of solvent. This is due to the fact that "cellulose molecules become surrounded by a sheath of hydrogen-bonded water molecules"[205], which "increases in size of about 5% radially, 12% tangentially, and 2% longitudinally"[206].

In oxidation, the cellulose molecule absorbs oxygen formed with the addition of chemical products, which will form other new groups, such as some acids. In turn, with this presence of acids, the hydrolysis of cellulose will occur. The oxidative degradation of hemicelluloses is identical to the cellulose reaction, but in a much wider way, because hemicelluloses have higher accessibility than cellulose[207].

Mainly, the hydrolysis and the oxidation are responsible for breaking the chain bonds, causing loss of strength in the cell wall polymers and its degradation.

The degradation is also linked to the effects of solar radiation on cellulosic materials. As radiation passes through the water it is absorbed as energy and dissipated by the polymer. This energy can produce a phenomenon of photolysis, in which the molecules dissociate causing an interruption of the chain links and a decrease of its length[208].

The photo-oxidation of cellulosic materials presents gaps in its propagation. It begins in the "amorphous regions spreading slowly to the well-ordered crystalline regions"[209] and for this reason lignin is the first to be degraded followed by hemicelluloses and then by cellulose. Because lignin is the substance with most amorphous regions it is the most sensitive to ultraviolet radiation. Absorbed energy causes oxidation which, in turn, creates hydroxyls and hydroperoxide radicals that attack glucose, reducing the physical and chemical properties of fibers, making them less resistant and soluble. The same thing happens to hemicelluloses, as oxidations reactions take place, and they rupture into monosaccharides, increasing their solubility. In cellulose, because it has two kinds of regions, crystalline and amorphous, it "does not

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[203] SCHEFFER, Theodore C. – Microbiological degradation... p. 52.

[204] *Idem* p. 52.

[205] KAYE, Barry – Conservation of Waterlogged Archaeological Wood... p. 36.

[206] *Idem.*

[207] YUAN-ZONG LAI – *Op. cit.* p. 497.

[208] TIMÁR-BALÁZSY, Ágnes; EASTOP, Dinab – *Op. cit.* p. 26.

[209] *Idem.*

appear to be a good absorber of ultraviolet light"[210], so the reaction will take longer to happen. When it does, it results in the self oxidation of the polymer, with the scission of the polymeric chain and the destruction of cellulose. The deterioration of cellulosic materials by photo-degradation affects the mechanical properties, truth chemical changes, basically giving rise to losses of strength and elasticity, as well as changes in the coloration of the materials[211].

Cellulosic materials normally do not have free radicals, but the absorption of UV light by sensitive groups produces the formation of radicals and the ionization of molecules, which accelerates the rate of physical and chemical deterioration. The free radicals are capable of initiating chain oxidation reactions that break away hemicelluloses, which protect from swelling and from chemical degradation; chemically alter lignin, changing its hydrophobic, mechanical properties and solubility, making it increasingly water soluble; and cause oxidation of cellulose, destroying the polymer chains.

In waterlogged environments the cellulose polymer is usually attacked by fungi, bacteria and insects, which can destroy the cell wall and induce mechanical disintegration. As cellulose materials are composed of various ratios of cellulose, hemicelluloses and lignin, with structures and chemical properties distinct from fiber specie to fiber specie, the result of the biological degradation will differ between them[212]. The microbial attack is retarded by the presence of lignin, *in vivo* lignin restricts pathogen invaders, acting as a physical barrier, because lignified cell walls are mechanically stronger than others, and also acts as a barrier against the microbial activities due to is resistance to digestion of cell wall degrading enzymes[213].

Also the quantity and diversity of the organism presented in an underwater site varies according to the season, sequence of marine species growth and environment.

The fouling organisms are the first ones to appear in an underwater archaeological site. They are responsible for the colonization process that will transform wood materials, and within these bacteria, fungi and mollusks plays the major role. After these appear crustaceans and mollusks, both quite destructive in terms of wood decay, as the tunnels and openings made by these marine borers induces loss of resistance and mechanical problems that can destroy the wood structure.

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[210] KRONKRIGHT, Dale Paul – Deterioration of Artifacts Made From Plant Materials... p. 157.

[211] PADFIELD, Tim – The Deterioration of Cellulose...

[212] BLANCHETTE, Robert A.; [*et al*] **-** Biological Degradation... p. 141-171.

[213] DEY, P. M.; HARBORNE, J. B. – Plant Biochemistry... p. 500.

The first element to be degraded by aerobic bacteria is hemicellulose followed by cellulose, remaining the lignin, which is slowly decomposed[214]. With this degradation, pores and cavities become even more filled with water and wood is transformed into a smooth and weak structure which is likely to collapse if wrongly transported or when it dries[215].

In the anaerobic bacteria there is a swelling of secondary cell wall, degradation of the layers S_2 and S_3 (which are in the crystal structure of the cell wall), exposure of the hemicelluloses to degradation, removal of the cell wall structure and degradation of cellulose, keeping only the lignin.

Within these forms of degradation it is possible, by analyzing the pattern of destruction, to distinguish the type of bacteria responsible for the decay, the most common being erosion, tunneling, cavitation bacteria and sulfate reducing bacteria.

The erosion bacteria, which are a facultative organism, will show depression holes that make the cell wall become thinner and friable. This is due to the ability of the bacteria to penetrate in the lumen and then go through the S_3 layer and access the secondary wall, where they follow the longitudinal cellulose microfibrill orientation producing depression cavities without disturbing the middle lamella that is maintained unaltered[216] (Fig. 9).

As for the aerobic tunneling bacteria, they present a pattern that looks like a network of tunnels. They start in the lumen, penetrate into the secondary wall degrading all its layers following through the middle lamella (Fig. 9), where after they spread to all the wood structure[217].

The cavitation bacteria, enter through the S_3 layer and penetrate by producing cavities within the S_2 layer, removing the cellulose and hemicelluloses in it, and going to the S_1 layer[218] (Fig. 9). The oxygen requirement for these bacteria is not yet known, but they do not appear to be common in extremely oxygen depleted environments[219].

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[214] The state of deterioration of waterlogged archaeological wood induced by bacteria was investigated. In this work it is possible to verify which are the elements more perishable see ČUFAR, Katarina [*et al.*] – Anatomy, cell wall structure…

[215] MODUGNO, F.; [*et al.*] - Analysis of lignin from archaeological waterlogged wood… p. 186.

[216] BLANCHETTE, Robert A.; [*et al.*] - *Op. cit.* p. 162.

[217] LANDY, E.; [*et al.*] - Bacterial diversity associated with archaeological waterlogged wood… p. 107.

[218] JURGENS, Joel A.; BLANCHETTE, Robert A. – Evaluating the wooden remnants… p. 394.

[219] *Idem*, p. 394.

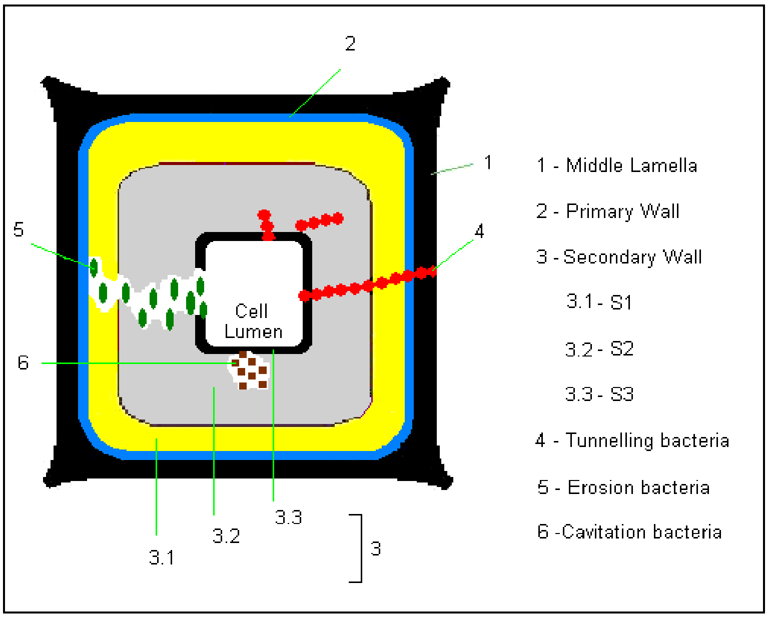

Figure 9 – Diagram of the Bacteria attack in cells f the wood. (Adapted from JURGENS, Joel A.; BLANCHETTE, Robert A. – Evaluating the wooden remnants… p.395).

Sulfate reducing bacteria are a distinctive group of anaerobic bacteria, which is not implicated in the primary degradation process, but dependent on simple elements such as carbohydrates. These are the same ones produced by erosion bacteria, during the degradation of the cell wall. The most important aspect of sulfate reducing bacteria is the ability to reduce hydrogen sulfide, which reacts with sulfur compounds, wood components, and also with cored iron forming iron sulfides[220].

Despite the severe effects on wood materials, such as the loss of structure or strength, the patterns are not seen in a macroscopic level, but it is possible to detect the attack by erosion or tunneling bacteria through a simple observation of the color of wood. The "wood degraded by erosion bacteria becomes very dark and shows extensive cracking of the surface layers"[221] and "wood with extensive attack by tunneling bacteria is only slightly discolored, usually to a light brown or light yellow"[222]. Also the presence of bacteria can be detected by paying attention to the smell of the sediments "as they give off distinctive odors (rotten egg smell)"[223].

As mentioned above, the submerged archaeological wood also suffers from fungi attack, which is much faster than the bacteria one. However it directly depends on

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[220] FORS, Yvonne - Sulfur-Related Conservation Concerns for Marine Archaeological Wood… p. 19-20.
[221] BLANCHETTE, Robert A.; [*et al.*] - *Op. cit.* p. 166
[222] *Idem* p. 66.
[223] JONES, Mark - *Op. cit.* p. 17.

the environmental conditions. Like bacteria, fungi degradation can occur in a very low oxygen environment, but they will not develop under anoxic conditions.

Basically fungi penetrate into the woody cell walls to get elements essential to their growth. They do this by producing extracellular enzymes (cellulases, hemicelluloses and lignin modifying enzymes[224]) that transform the structural wood polymers into sugar and other compounds.

Based on their specific morphological features of attack it is possible to recognize the types of fungi, because like bacteria, they also present distinctive patterns. The most common fungi in waterlogged wood are the white and soft rot.

The white rots cause cell wall degradation by penetrating into the lumen progressively degrading the interior and exterior of the cell wall. In an early stage, the lignin and hemicelluloses are the first elements to be extensively degraded, remaining the cellulose, which in the long-term is also destroyed later[225].

In terms of patterns it is possible to identify erosion and, in some cases, a large quantity of cavities, that look like honeycomb holes. This will turn wood in a very unstable material with an increase of pores throughout the cell, thus a higher capacity for water absorption[226] which will lead to losses of dimensional stability and changes in shape. In a macroscopic level, it is possible to recognize a spongy appearance and, depending on the type of white rot, changes in the original color with a "bleaching" effect, due to a higher proportion of cellulose content; and brown, red or violet color appearance, due to lignin decomposition products[227].

Soft rot fungi also act through continuous enzymatic activity, but in this case lignin is only modified in a later stage of the decomposition, the first ones to be destroyed being cellulose and hemicelluloses.

In this kind of degradation two different types of decay can appear, one that produces cavities and another that forms erosion. Both start at the lumen, but the first one, matures and produces cavities, within this grow S_2 and S_1 layers are affected, with

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[224] For a better understanding of polysaccharides degraders upon wood cell wall and lignin degrading enzymes see EATON, R. A.; HALE, M. D. C. – Wood: decay, pests and protection… p. 163-169.

[225] BJÖRDAL, Charlotte G.; NILSSON, Thomas - Waterlogged archaeological wood...

[226] HON, David N.-S. – Preservation of Waterlogged Wood... p. 809.

[227] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke. – *Op. cit.* p. 103-104.

a minimal attack on the S_3 layers[228]. The erosion soft rot fungi involve the complete decay of the secondary wall layer, but no degradation of the middle lamella[229].

Because soft rot begins the attack from the surface into the interior of the wood the destruction will happen in the superficial layers of wood, giving it an appearance of a soft and smooth surface[230].

Despite having a natural resistance to microbiological degradation, wood materials are not entirely protected to this attack, which manifests itself in a chemical way, corresponding to the decrease of mechanical strength, stiffness, changes in color and in the fragility of the fibers.

Biological decay also comes from other organisms like marine borders, such as mollusks and crustaceans. Molluscs, specially *Teredinidae* (ship-worm or *teredo*), have a severe degradation effect as the larva penetrates the wood and drills, in a longitudinal direction and irregular course, circular burrows forming a calcareous deposit (Fig. 10), producing tunnels 450 mm in length and 40 mm in diameter. By making these openings it induces mechanical problems that destroy the wood structure. Since *teredo* is able to live and settle in a saline environment or in freshwater, this attack occurs in seas and oceans worldwide, and the spread of it depends only on water temperature and on the resistance of the wood species.

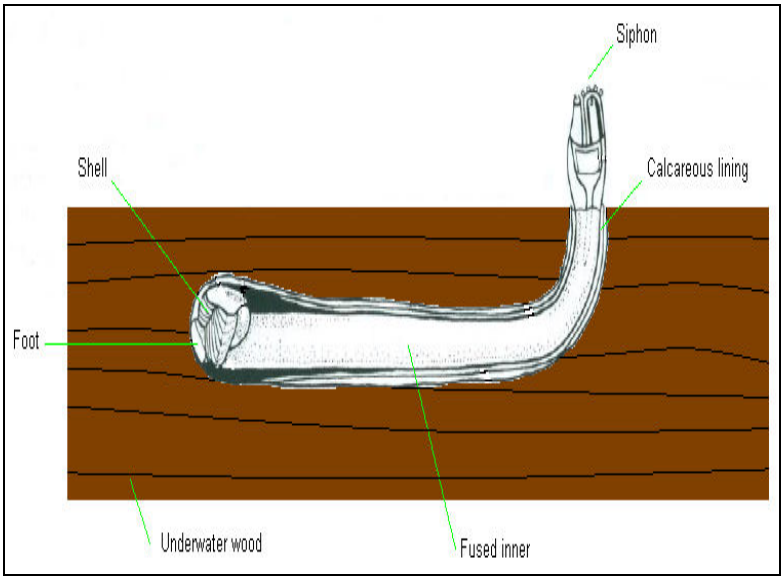

Figure 10 – Diagram of the *Teredo sp*. attack in underwater wood.

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[228] JURGENS, Joel A.; BLANCHETTE, Robert. A. b) - Characterization of wood destroying microorganisms…

[229] SINGH, Adya P. – Micromorphological characteristics of wood biodegradation... p.142.

[230] PALA, Helena - Constituição e mecanismos de degradação biológica… p. 61.

Martesia striata, the most known of the Pholadidae, are also mollusks, but they are a family of bivalves similar to a clam (Fig. 11). They penetrate and grind away into wood creating tubular burrows that can achieve 5-10 mm diameter, with a length 3-8 times the size of their shell. The hardness of the wood and the density of the mollusk population both influence the growth rate and size of these organisms. They stay in their burrows during their lifespan and when they die they leave an empty tubular burrow that other marine life may use. They are mainly found in tropical and subtropical waters.

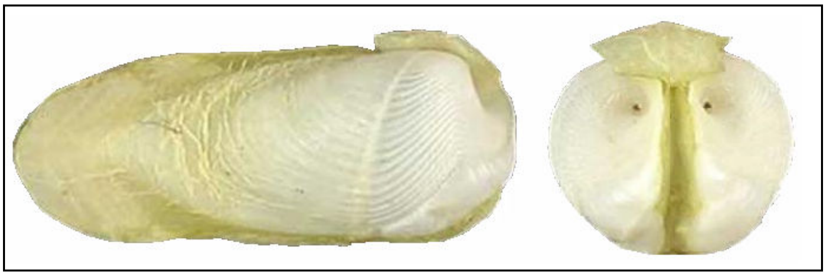

Figure 11 – General aspect of the *Martesia striata*.(Adapted from GOETHAELS, Rika; DE DONDER, Fernando - De Donders Shells…)

Being the most harmful for waterlogged wood, crustaceans belong to a large group of aquatic invertebrate animal that are protected by a calcified exoskeleton with a conical body. This includes *Limnoria* and *Sphaeromatidae*, from the Isopoda order, the *Cheluridae*, member of the Amphipoda and barnacles that belong to Thoracica superorder.

Limnoria are the most destructive crustaceans: they feed on the cellulose by producing cellulases. In the search for a source of food they start by colonizing the surface layer of the wood where they make holes (until 2mm diameter), and after that they progress to the inner layers. Despite being small, 1–4mm size, it is possible to see them due to their white or gray pale color (Fig. 12). The elements of this family can live in environments with a large range of temperatures that goes from moderate (*L. quadripunctata*), cold (*L. lignorum*) or temperate and cold (*L. tripunctata*).

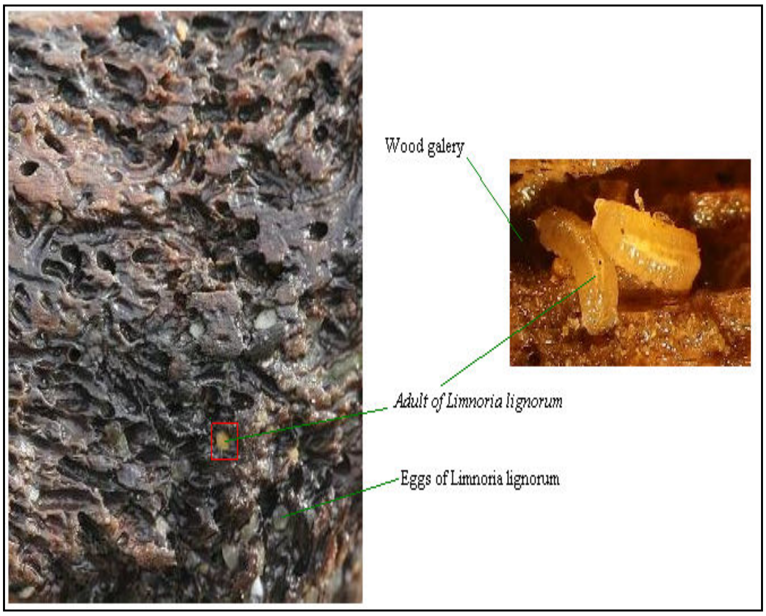

Figure 12– Aspect of wood attack from *Limnoria lignorum*. (Adapted from FENWIK, David – Aphotomarine…).

Sphaeromatidae act mainly in the tropics, where they can reach 10mm length and 6mm diameter. They attack wood by making cavities, leaving a honeycomb pattern.

Amphipod family can be found in almost every kind of aquatic environment. They are known to decompose organic matter. In the case of *Cheluridae*, only the superficial layer of the waterlogged wood materials are degraded, in fact, they use the *Limnoria* tunnels enlarging it but they do not enter deeper into the wood. *Cheluridae* are very small with 1-3mm size with a translucent color.

The presence of metals will also affect biological degradation rate as well as the chemical stability of the archaeological waterlogged wood and its mechanical strength. Nevertheless, interaction of waterlogged wood with metals is dependent on wood species, moisture content, environmental conditions and the nature of metal. Normally the metal corrosion products replace water and plug the voids in the internal wood structure, giving strength to the cell wall through a bulking process[231].

Concerning biodegradation, this can happen according to the metal to which it is exposed. If copper is impregnated in waterlogged wood, then as this metal is quite toxic the wood will be protected from aerobic biological attack[232]. If it is iron and even in an anoxic environment waterlogged wood can be found deteriorated[233]. This is possible

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[231] MACLEOD, Ian; RICHARDS, Vicki L. – The Impact of Metal Corrosion Products... p. 331.
[232] *Idem*, p. 345.
[233] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke. – *Op.cit.* p. 46.

since this metal creates a pH range that enables the development of sulfate-reducing bacteria[234], a situation that affects not only the wood structure but is also a concern during conservation treatments[235].

About the decay of the different species, and despite all the differences in chemical composition and in permeability, the degradation behavior of waterlogged wood is quite similar in hardwood and softwood, the difference only lies in the extent of it and how quickly it occurs. In both, the swelling of the S_2 takes place with the hydrolysis of hemicelluloses and the loss of the cellulose, and as a result the crystalline structure is broken and the cell wall degrades, leaving just the residual lignin. After time the lignin also degenerates increasing the voids in the cell wall, thus basically "the wood becomes more porous and permeable to water and the cell cavities and intermolecular spaces fill with water"[236]. Considering these similarities, and to better understand the deterioration process regarding the different species it is, also, better to reflect on the permeability of the wood, which is related, not only to the chemical compounds, but also to the radius of capillary, density and specific gravity of wood.

Underwater archaeological oak usually shows a selective degradation, with loss of carbohydrate and with the physical degradation of biopolymer[237]. Studies on Portuguese oak found that it has little elasticity, tensile strength and a very low axial bending[238], thus it has little ability to resist stress and mechanical shocks. Hence, if the oak is waterlogged this means that it will be even less resistant to handling.

As for pine, it presents a heavy destruction of the cell walls due to the reduction of wood components. Despite the lignin content being slightly higher in pine rather than in oak, in pine this element does not resist a waterlogged environment and it even resists less than the lignin in oak. With the loss of lignin, as well as other sugar components, porosity increases, and the more it does, the more water enters, destroying all the cell structure.

In an underwater environment there is the possibility of woody materials remaining in relatively good condition, with the fact that the water occupies cellular spaces, capillaries and micro-capillaries avoids oxygen going into pores, allowing

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[234] SANDSTRÖM, Magnus; [*et al.*] c) - Sulfur accumulation in the timbers...

[235] After been restore with PEG large amounts of sulphur compounds were found in *Vasa* wood, the analysis performed have shown that linked with this situation were iron compounds. SANDSTRÖM, Magnus; FORS, Yvonne; PERSSON, Ingmar - The Vasa's New Battle...

[236] HAMILTON, Donny L. c) – Conservation of Cultural Materials... p. 306.

[237] HEDGES, John I.; [*et al.*] – Degradation of carboohydrates and lignins... p. 701-711.

[238] RAMOS, S.; [*et al.*] - Potencial Tecnológico da Madeira de Quercus faginea Lam… p. 443.

relatively good conservation. Nevertheless, it is possible to find waterlogged wood in what appears to be a good external condition, but in fact the material is much weaker than it seems and it may even collapse if handled. Another aspect is that with excavation these materials are exposed to a new environment and to organisms like mollusks which, in a few weeks, will attack and affect the strength of these materials.

14.5. Flax, hemp, ramie, cotton, sisal and coconut fiber

The way the cellulosic materials are degraded is very similar, although it appears that the cellulose fibers percentages and destruction rates are slightly different from each other, such as the case of flax and cotton. Flax survives much more easily in an underwater archaeological environment than cotton, and the explanation lies in the number of crystalline and amorphous regions available. In flax, crystalline regions are proportionally greater than in cotton, therefore the water cannot connect so easily with the bast fibers. It does not mean that they do not degrade by the action of hydrolysis, but this will take longer, especially when considering the initial increase of strength and elasticity of these fibers when wet[239].

Cotton fibers easily absorb water, increasing by about 40%[240] when in an underwater environment. In this situation a greater number of links between the amorphous areas and water are formed, hence it is easier for cotton fibers to become hydrolyzed.[241].

A similar phenomenon occurs with the hydrolysis of sisal as its fibers become very brittle when in contact with water, becoming easily hydrolyzed.

In contrast, other fibers such as hemp, ramie or coconut have great physical and chemical resistance, both to water and chloride. Despite this durability, it is found that when subjected to continuous cycles of drying / wetting these elements become more fragile and perishable[242].

In terms of reaction of the material to pH variation we must point out the reaction of flax and cotton. Flax appears to be quite resilient when subjected to acidic or slightly alkaline environments: however, it is deeply attacked by strong acids or weak

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[239] COOK, J. Gordon – *Op. cit.* p.10.

[240] TIMÁR-BALÁZSY, Ágnes; EASTOP, Dinab – *Op. cit.* p. 35

[241] *Idem* p. 34.

[242] SAVASTANO, Holmer – *Op. cit.* p. 6.

acids, especially if subjected to increased temperature. The cotton fibers present excellent resistance to alkaline environments, but in the presence of a strong acidic environment they are easily degraded under the acidic hydrolysis giving rise to hydro-cellulose.

If metallic materials are near they can lead to a faster degradation of the cellulosic materials. In fact, if iron is present, a high concentration of iron corrosion products arises, causing an anoxic environment, in which "salts are converted into sulfides"[243]. Also, corrosion products cause damage to cellulosic fibers due to "physical swelling of the corrosion products through changes in hydration states and crystallinity"[244]. More damage is induced by iron salts, abrasion, and compression of the material or, most of the time, the inclusion of mineral, which enables the viewing of the material's original form. And if copper and its alloys are present, cotton fibers are degraded.

In terms of biological degradation, also observed are substantial differences in the strength of materials. The first attack of fungi and bacteria occurs in the amorphous regions of the primary fiber wall, spreading out to the crystalline areas, following the direction of the secondary wall[245]. As stated earlier, flax does not present as many amorphous regions as cotton; hence it tolerates better biological attacks, both by bacteria and by fungi.

At the level of lignin and in terms of resistance to microbial attack of the fibers, ramie, for its large amount of lignified cell walls, is the most durable followed by flax.

15. Discussion

Degradation of organic materials results from physical actions or chemical reactions, induced by the underwater environment itself (strength of tides, temperature, salinity, pH, light) and by (micro) organisms (marine borers, bacteria or fungi).

Rivers present major quantities of organic compounds, which along with low levels of oxygen promote anaerobic environments, and thus induce anaerobic bacteria attack. In a sea or ocean the major degradation is caused by physical stress or by marine

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[243] KAYE, Barry – *Op. cit.* p. 36.

[244] GODFREY, Ian; KASI, Kalle; RICHARDS, Vicki – Iron removal from Waterlogged Leather and Rope... p. 439.

[245] TIMÁR-BALÁZSY, Ágnes; EASTOP, Dinab – *Op. cit.* p. 36.

borers. Nevertheless, when oxygen levels are high, oxidation processes take place, and aerobic degradation occurs. In turn, this decomposition of the organic material has the ability to induce nitrification by aquatic organisms, and also the chemical oxidation of substances such as metal ions that will promote the loss of oxygen and transformation into an anaerobic environment, in which only anaerobic bacteria are able to survive.

The attack caused by fungi or bacteria can take years to completely destroy an object, but degradation by hydrolysis, oxidation or marine borers can happen in a faster way.

CHAPTER IV – FROM EXCAVATION TO DISPLAY: CONSERVATION PROCEDURES

In order to protect and preserve underwater heritage, several circumstances should be considered, such as the environment and nature of waterlogged organic archaeological remains. The right environmental circumstances such as water temperature, small amounts of dissolved oxygen or free oxygen, dissolved minerals, acids and sedimentation make preservation of organic artifacts possible[246]. However, this situation is not always achieved and even the site environment can change, which means uninstalled or degraded materials which, sometimes, are not easy to identify. Also, the equilibrium of these wet sites is compromised if any physical disturbance occurs, since underwater archaeology is, at first, a process of discovery and excavation; this means that any archaeological intervention must be very well considered.

Another aspect is that waterlogged sites can occur in a variety of different areas, such as oceans, rivers, lakes, dams or any other water bodies with which people interact, meaning that each site will present its own complexity. Hence it is so important to consider the type of site before excavation. This not only will help to understand the burial conditions, but also will allow to better predict the conditions and the type of materials that can be found, which in addition enable better preservation measures for the artifacts.

Also, organic materials present great challenges to conservation, as once excavated and subjected to a new environment, deterioration begins. This degradation will happen much faster if the organic artifact is removed from its waterlogged environment and exposed to the atmosphere. It begins to react by drying out, shrinking, cracking and warping, and unless on-site conservation steps are taken to control this immediate deterioration occurs.

The most important issue in preservation is to elaborate, from the beginning of the underwater archaeological project, a conservation strategy. This should incorporate procedures based on materials, decay, lifting techniques, conservation goals and level of treatment required. Considerations about display or storage also need to be addressed. All these steps ensure that organic artifacts will not collapse once they have been disturbed or when exposed to new environmental conditions, and mishandling must also

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[246] The action of water and other elements are not always destructive in fact some environments can act as preserves, JEWELL, Donald P. - Fresh-Water Archaeology... p. 414-416.

be avoided, either during the recovery from the site or during their analysis, as well as guaranteeing their stabilization.

16. The excavation process and on-site preservation measures

As is well known, as in the case of terrestrial archaeology, underwater excavation is a destructive process of investigation. The excavation project should be carried out taking into account that it is an unrepeatable process, which deals with cultural heritage that is finite and non-reversible involving substantial data gathering, where unpredictable variations affecting the materials, can occur. Hence it is indispensable to ensure that adequate measures are provided, beginning with site exposure and on site-conservation.

16.1. Project planning

In any underwater archaeological excavation, collaboration between specialists should be planned from the beginning of the project. This implies a conservator, as well as a remote sensing specialist, divers, biologists, geophysicists, and other specialists or advisers. This is an appropriate strategy, as they can help through research and provide assistance during the different stages. Also, during planning, it is essential to inform all the interveners about the initial planning stage of each working team, its working methods and protocols. At this stage, information about the type and possible state of preservation of materials likely to arise is also important to be given.

Whereas excavation, waterlogged terrestrial or in an underwater site, is costly this means that all these areas must be included in a budget plan, with defined timescales and goals. Furthermore, this approach allows a better cost control.

Besides staff, the funds for underwater archaeological excavation should include facilities, labeling materials, recording, lifting, wrapping, cleaning, storage on-site, packaging or transportation, and post-excavation analyses (for archaeological and conservation investigation), conservation treatments, storage or display.

16.2. Baseline studies and data recording before excavation

An underwater environment is extremely dynamic and organic materials are really perishable. Also, considering that all kinds of degradation can occur in an underwater site, the most harmful being biodeterioration and physical damage, from wave and sand movements, this means that any disturbance to the site, which usually corresponds to an increase in oxygen, water contents, nutrients and biological exposure, will lead to a more aggressive environment. Because of these environmental changes, conservation must begin before the excavation starts. In fact, this is the best opportunity to collect data, with which it is possible to predict the nature of possible finds as well as their preservation conditions. Moreover, this information is crucial to develop a future conservation treatment or an *in situ* storage.

Featuring an underwater site is very complex, detailed measurements of chemical, physical and biological parameters being necessary. These data collection is a critical element of the project. In order to fulfill these requirements and to analyze threats to the archaeological materials it is necessary to have an assessment of several data such as: sediment dynamics, pH, redox potencial (E_h), salinity and biological activity.

In this survey, it must also be considered that these items are directly related to each other. Sediments analysis is crucial for understanding how long the archaeological material was exposed, the time that it took sediments to cover the site and after that deposition, if there were movements or erosion of it. On the other hand, the pH of the sediment has a direct influence upon the E_h. The E_h and the temperature can directly influence bacterial activity, which makes it much easier to identify the different organisms and the extension of decay. Also, the presence of oxygen indicates the type and growth of colonizing organisms[247].

Due to this relationship, the most important item to be measured is the E_h. Through this, the chemical behavior of the underwater environment, the dissolved chemical species[248] and also the profile of the sediment as well as the archaeological layers are characterized[249]. To access the redox potential the electron availability in sediment is measured, determining its oxidizing-reducing nature. Usually marine

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[247] GREGORY, David b) – Re-burial of timbres in the marine environment ... p. 344.

[248] LILLIE, Malcolm; SMITH, Robert a) – International Literature Review: *In Situ* Preservation ... p. 27.

[249] HOLDEN, J. [*et al.*] - Hydrological controls of in situ preservation ...

sediments present three distinct zones: an oxidized zone at the surface, related to high levels of oxygen, which means positive redox values; a reduced zone, in a deeper level, which is usually anaerobic, thus, with negative values; and a transition area, between the two[250]. In order to proceed with E_h study numerous investigations have been done, however the most accurate method is the use of standard hydrogen electrode that calibrates another standard cell, which in turns measure the loss or gain of electrons from a platinum electrode[251].

The pH of an underwater archaeological site also depends on the type of artifacts contained in the burial context, and it will be very important to develop *in situ* preservation. For *in situ* pH measurements, the most precise way to do it is through the retrieval of samples with a hand probe with several cm depths, without disturbing the site, and proceeding with the measurements at a laboratory with a proper standard method for wet soils[252].

As stated before (micro) organisms are the most responsible for the decay of organic materials. The rate depends upon the amount of organic material available, the type of organisms and the environmental factors. Due to this, the research is done through these elements, which leads to a type of activity, or by introduction of several organic samples in the site[253], which are observed by different microscopic techniques, providing information about the deterioration.

The frequency of data recording is particularly important to correctly characterize the burial environment. To have a good study, weekly analysis should be done. However, one should also take into account the difficulty, in some periods of the year, to access the site, the facilities and equipment available for research, as well as costs. All these aspects can be viewed as constraints, hence monthly basis measurements are considered the minimum required to obtain the site profile.

This does not mean that conservation comes first before archaeology, but rather it provides a collaborative action, which helps to identify materials that may exist and to characterize burial conditions.

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[250] GREGORY, David – *Op. cit.* p. 345.
[251] *Idem.*
[252] MATTHIESEN, H. a) - *In situ* measurement of soil pH… p.1373 - 1381.
[253] BJÖRDAL, Charlotte G.; DANIEL, G.; NILSSON, Thomas - Depth of burial… p. 15-26.

16.3. Protective measures while excavating

As a result of permanency in a particular environment, archaeological materials experience changes, which tend to be increasingly slower as the artifacts come into balance with it. However, the discovery of an artifact involves the interruption, in an abrupt way, of that relationship. In the same way the excavation requires materials to face physical stress, posed by water dredge or airlift, as well as a new environment, organisms, tides and flows, meaning new conditions and hazards, causing a sudden increase of the rate of decay.

In order to minimize the excavation impact, preliminary stabilization may be considered. In addition an action protocol should be implemented. This protocol must ponder the difficulty of working on an underwater site (lack of visibility, depth, and cold temperature) and the need to use equipment compatible with the archaeological materials and the environment.

The first step applied to all underwater organic materials is to remove only a part of the sediment that covers it. This will give the shape, size, components and an idea about the preservation state of finds, which is enough to collect data and to inform about the possibilities of handling and lifting. As it is not a very invasive approach, the archaeological context is maintained, allowing the archaeologist a complete overview of the site, continuing with the record and numbering of every object.

In this task some materials and procedures must be considered: the use of a net filter in the airlift or dredge; the placement over a small and sensitive area of a vented nesting container or the covering of the artifact with it, and only then the use of the underwater excavation equipment; or, if the material seems to resist the placement of weight, the laying of sandbags. All these items are easy to take to the underwater site, simple to use and to set aside during the excavation.

For excavation tools like trowels, soft-haired brushes are also suggested. Another technique recommended is the use of hands while excavating, this is the best way to feel the materials and also, with gentle waggling movements, to dislodge sediments[254].

As seen in the preceding chapter it is very important to know how the different materials react when in water. When excavated, ivory is very difficult to distinguish

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[254] Adequate planning and logistical support as an example see UNDERWOOD, Chris – Excavation Planning and Logistics… p.154-155.

from bone, however, the first presents a laminated structure and is much whiter, denser and smoother than the second. As for leather, it is likely that its internal strength has been lost, so while in excavation it is likely to appear as gelatin or in a very fragile situation and must be excavated with extreme caution. The same for textiles made from keratin, fibroin or cellulosic fibers which will be in a very delicate condition. Thus the excavation must be done with great care, and the sediment close to it should not be removed. If wood is found, probably it is degraded and fragile, especially small objects.

To better prepare the construction of litters and tanks, and to understand the extension of wood decay in a reliable way, tests should be carried out. A simple and easy way to get the required data is by performing an *in situ* exam with a Pilodyn. This is a minimally destructive tester that by firing a pin into the wood, allows the calculation of the resistance and density of wood, and then the extent of deterioration, even by shipworms[255]. If penetration is greater than 40mm, the depth of deteriorated material can be considered extensive[256]. Conversely, if there is little penetration (10mm or less) deterioration is minimal.

Composite objects are difficult to analyze in a waterlogged environment. They must be treated with caution, as they usually tend to break in the contact zones between the different materials. Usually textiles, leather and wood adhere to iron objects and cordage is often found held together with wood.[257]

If encrustations are present in the artifact they must not be removed, as data may exist inside it, and also they act as a protective barrier[258].

In order to take record of artifact finds labeling is usually performed. Deemed as a necessary technique it is, in most cases, difficult to carry out on organic materials, as they are very sensitive to handling and to materials used as labels or tags. If during the excavation the artifact is in a poor preservation state, labeling can be done through an indirect system by placing identification alongside.

The choice of the method used for protection during excavation or for labeling will vary according to the site and material requirements and, probably, will differ depending on the compromises needed to be made between keeping the artifacts exposed in the original place and available for the archaeological investigation and its preservation state towards different environment conditions.

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[255] GREGORY, David; [*et al.*]- A preliminary assessment of the state of preservation…

[256] CLARKE R. W.; SQUIRRELL, J. P. - The Pilodyn… p. 182.

[257] RODGERS, Bradley A. – *Op. cit.* p. 198.

[258] HAMILTON, Donny L. d) – Field recommendations…

16.4. Lifting and handling

A find should not be simply removed from the underwater archaeological site without proper justification[259]. Due to the fragile nature of organic materials and in the best interests of the archaeological investigation the choice, generally, involves a conservation treatment and, therefore, the removal from the archaeological site.

Until artifacts are sent to a conservation laboratory they need to be suitably kept, which implies planning proper lifting, on-site conservation, packing and transportation.

Waterlogged organic materials can be very soft and friable, because of this and due to fact that they have to "bear their own weight but also (…) the water with which they are saturated"[260], for the lifting they must be handled as little as possible.

Since the sediment can be the element that holds together the fragmented object (especially for leather and textiles), and because *in situ* it may be difficult to understand the complete object, so the surrounding sediment should be kept and lifted together through the *block method*. Sediments containing the object and a few centimeters margins around are isolated, on those is placed a rigid container and underneath slid a bigger piece of a rigid material (Fig. 13). Then, everything is placed into a rigid support, like a nesting container, and lifted.

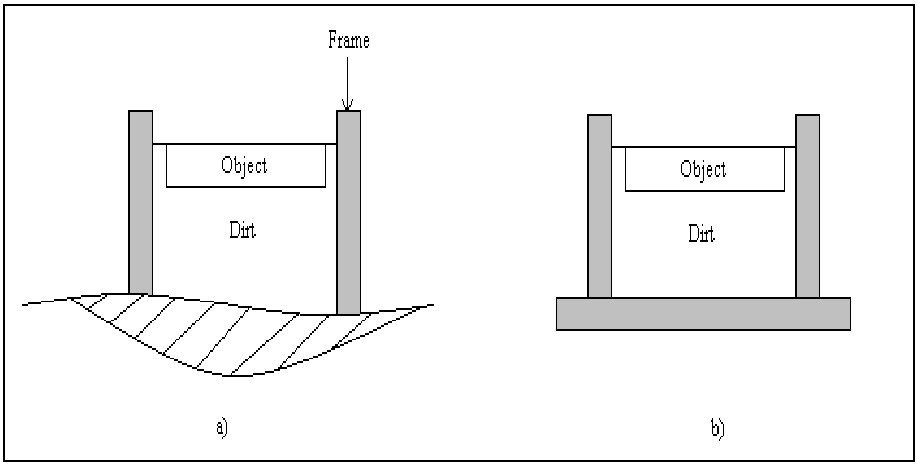

Figure 13 – General lifting procedure (A - First stage, B - Second Stage). (Adapted from SEASE, C. - First aid… p.38.)

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[259] UNESCO - Convention on the Protection of the Underwater Cultural Heritage UNESCO Paris, 2 November 2001. Article 2.5.

[260] ROBINSON, Wendy – First Aid… p. 88.

If the organic material appears to be in a sound condition, it does not mean that care should not be taken. If it appears to resist handling, the method that can be used is wrapping, as long as the wrapping material does not damage the object and it can be easily removed later. In this approach long polyethylene strips can be used as a bandage, securing the ends with rubber bands, and tighten or put them inside a rigid support (Fig. 14, 15). In the case of large timbers, aluminum ladders can be used, as long as they are well wrapped with foam.

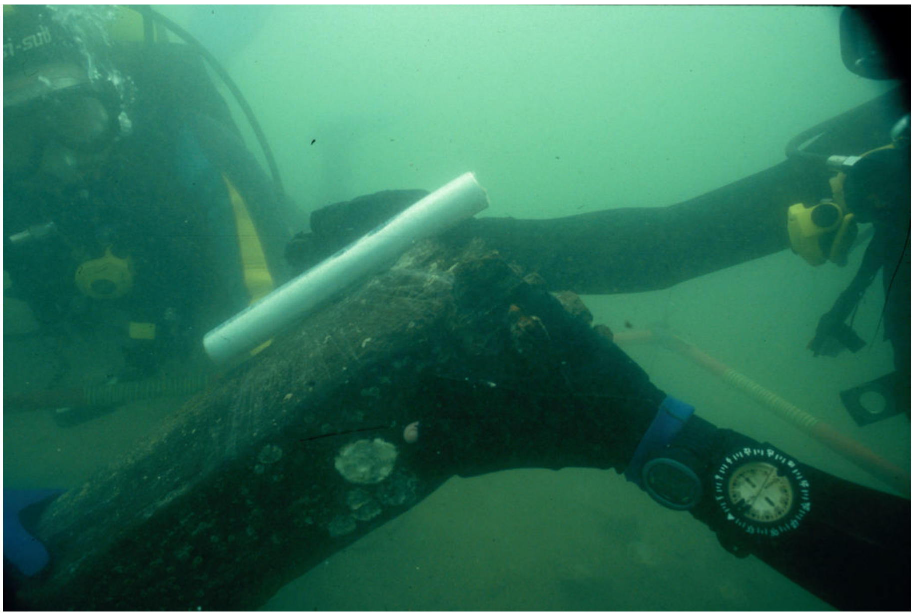

Figure 14 – Wrapping a frame with polyethylene.

Before lifting, all the archaeological materials, supports or containers should be well identified through labels (Fig. 15). Also all the materials and associated supports must have structural strength.

For the lifting, experienced professionals are needed. The usual technique is airbags or mechanical methods, such as hoists or winches[261], but if needed other methods can be applied.

As soon as the objects reach the surface and until they are transported to the treatment facilities, they must be taken to a reception area created for the purpose of maintaining them in wet conditions.

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[261] *Idem.*

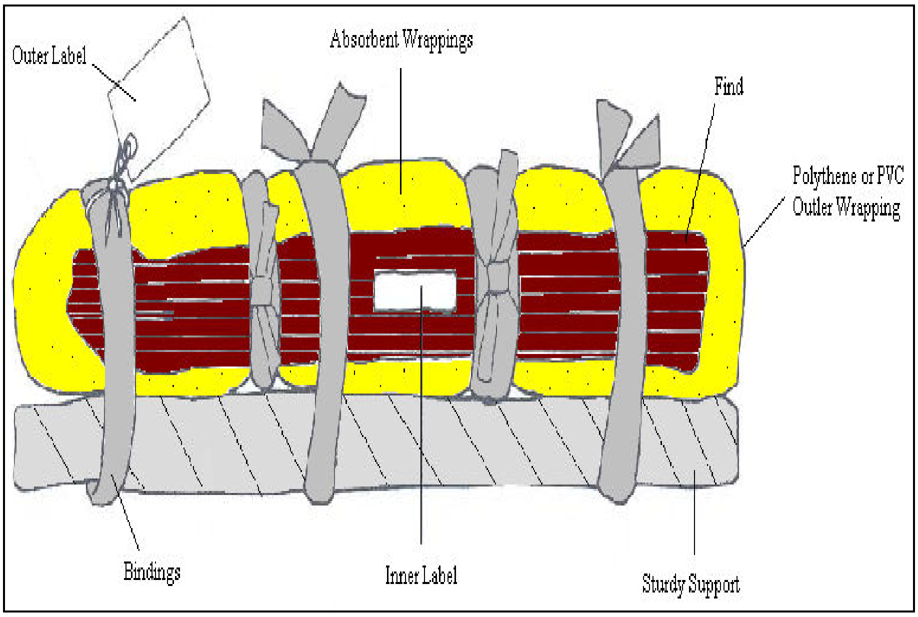

Figure 15 – Sturdy support before being raised. (Adapted from ROBINSON, W. - First Aid… p. 90).

16.5. On-site preservation storage

Once the artifacts are lifted it is essential to avoid contact with a new environment otherwise they will perish. It is necessary to choose an area for storage with proper conditions. If there is a conservation laboratory or a museum, with adequate means and a conservator near the underwater archaeological site, the finds must be transported and treated in those facilities. If such premises are not available, the finds must be stored in the nearest available place that will serve as a field laboratory.

This laboratory must have wet and dry areas. The first will be for examining objects, the second for documentation and research, and both with suitable equipment and conservation materials.

As for the equipment there must be lifting equipment and trolleys to safely move objects during records, documentation and treatments. Temporary tanks and containers, of all sizes with and without lids, are also indispensable, serving both to desalt and to store. Good cleaning/washing instruments with fresh water or a large sink for rinsing together with a reliable water source is also recommended. Equipment to measure salt content, a low-power binocular microscope for a good analysis of the materials, weighing scales, and recording equipment for registration is also suggested. Finally, if organic material appears to be very fragile, a refrigerator for cold storage and a power supply[262] is advised.

Concerning supplies, polyethylene bags, sheets or “bubble pack”, for packing and protecting finds against desiccation and transportation stress, along with absorbent material such as synthetic sponges will be needed. Measuring cups, plastic buckets and plastic bottles to hold solutions, graduated cylinders and plastic beakers to make solutions and pH papers to control solutions are required.

A set of tools is also required: small spatulas, wooden or plastic sticks, pins or needles, a variety of brushes, sprayers, tweezers, scissors and plastic tubes. Many others can be used but it all depends on the work to be done in the field.

For labeling artifacts the use is advised of resistant materials that present long-term aging qualities, not damaging the objects even when removed. Acrylic labels or other waterproof labels (Plastic tape labels or Teflon sheet[263]) can be used along with waterproof marker pens.

In addition to the above, to avoid biological degradation the use of biocide and fungicide chemicals must also be considered. The chemicals chosen must not interfere with the materials future analysis (especially radiocarbon dating) or conservation treatments.

As for conservation measures, they must start with a Condition Report, i.e. an evaluation of the preservation state of each artifact, describing the type of material, treatment method used in the field season, chemicals used and observations about treatment failure and/or success. This allows the establishment of a chart identifying all finds rescued and treatments to be developed on-site, with attention being paid to the designation of the most urgent cases (Table 2). Usually, the underwater archaeological artifacts show differences in their stability, the most perishable being textiles, dye textiles and leather followed by composite materials, wood and ivory, with bone being the most stable (Table 2).

Besides this information, archaeological objects must be individually recorded and documented with a full and well organized description of the day of lifting, packing measures for lifting, transportation from the site to the field laboratory, treatment carried out on-site (properly dated), and transportation from on-site storage to laboratory, and warnings or any details that could be considered important. During the finds evaluation

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[262] JONES, Mark – *Op. Cit.* p. 9.

[263] PEARSON, Colin – On-site storage and conservation... p.107.

it is important to always keep them wet. In this description, analysis about the artifact's construction, decoration or sections that compose the object must be outlined.

Table 2- Rescue and treatments of finds to be developed on-site

Level	Type of finds	Attention
1 (Highly unstable)	Dye materials, leather, textiles, sailcloth	Deterioration occurs within a few minutes of exposure to light and air; active treatment immediately is required.
2 (Fairly unstable)	Organic materials with concretions	Deterioration occurs in hours; material must be kept wet.
3 (Moderately stable)	Wood and ivory	Must be kept wet; if in a passive storage bacteria and fungi attack must be prevented; storage with cold temperatures can be used.
4 (Long-term stable)	Bone	Keep wet and desalinate.

(Adapted from JONES, Mark, ed. - For future generations… p.10).

Once the evaluation and description are done, artifacts must be stored according to the nature of each, in tanks or in small containers, completely immersed in water. If they are too large to fit into a storage tank, they must be kept wrapped and protected from drying until transported to a proper conservation laboratory or until a suitable storage tank is made[264].

Since storage can take a few months it must be checked every month, to ensure that the contents are still wet and free of fungal growth. This is mainly considered a passive treatment once no major intervention is intended to be carried out.

In some cases to better understand the details of construction, decoration, nature (in the case of composite materials) or to analyze the preservation state of the object, it is important to proceed with cleaning. For the general removal of sediment, mud or silt, a gentle wash can be done. Proper cleaning equipment can be used, as well as a large diameter hose (2cm to 4cm) with tap water, running without pressure. In both cases the organic artifact's surface must be protected by polyethylene mesh and the end of the hose should be held just above the surface (Fig. 16). It is also useful to use fingertips to prevent water pressure affecting the object's surface directly. Since mechanical cleaning is an irreversible process, this involves the removal of surface sediment and other

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[264] ROBINSON, Wendy – *Op. cit.* p. 13.

alterations; it must be approached with caution and always considered as a procedure to be carried out as an exception.

Finds made of cellulosic textiles or leather are very likely to deteriorate when exposed to light, so they must be kept away from it[265]. Also, in an environment with light and even with the addition of a biocide or fungicide, microorganisms can grow and cause material destruction. For these reasons light levels must be low, thus, tanks or containers with lids in dark colors are recommended or if they have no lids they must be placed in the shade.

High temperature can also damage organic archaeological materials, especially if they were found in a low temperature environment. Cool temperatures delay the decay rate promoted by the microorganisms, materials like leather, cellulosic textiles, wool, silk or hair should be kept cold or refrigerated.

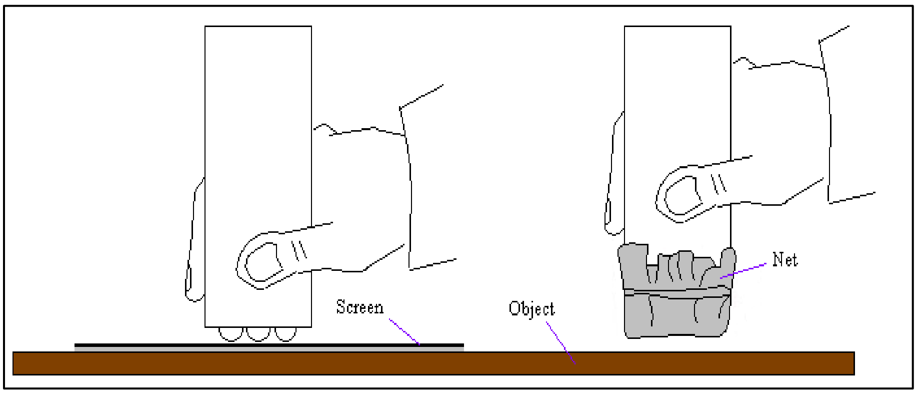

Figure 16 – Cleaning method. (Adapted from NORTON, Ruth E. – Conservation of Artifacts… p. 217).

The best on-site storage should also take into account the oxygen level, which has to be kept as low as possible, therefore the tanks should be designed as deep as possible[266].

On-site storage of organic materials demand constant surveillance, however their maintenance is just by passive treatments, easy to perform, being safe to proceed and economically feasible. On the other hand, as heritage elements they should be accessible to any investigation.

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[265] *Idem.*

[266] KEENE, S. – An approach to the sampling and storage... p. 9-11.

17. Intervention criteriae

An underwater archaeological site is a heterogeneous mixture of different materials with distinct friability and permeability properties. Considering this and the fact that different objects present different requirements and that “you cannot preserve what you don’t know”[267], the first moment of an intervention should be materials analysis and function, followed by the degradation processes knowledge, the evaluation of the conservation state, the treatment aim and its conservation.

Conservation treatments should allow balanced solutions, capable of answering preservation needs and always enabling archeological research. Concerning this need, a multidisciplinary compromise should arise, mainly when required treatments involve a higher level of intervention.

17.1. Terminology and definitions

For a better understanding of the general principles and ethics of conservation the terms preservation, conservation, preventive conservation and restoration need to be summarized. According to the International Council of Museums Committee for Conservation (ICOM-CC) preservation is all the actions taken to slow down or prevent degradation or damage to the cultural heritage, either by controlling the environment or by proceeding with structural treatment[268].

As for conservation, it is defined by all the interventions aimed at safeguarding tangible cultural heritage, ensuring its accessibility to present and future generations. Conservation also includes preventive conservation, which are all indirect "measures and actions aimed at avoiding and minimizing future deterioration or loss"[269], reducing hazards by controlling the environment, display and storage. Despite not interfering with cultural objects appearance these actions are able to delay degradation processes or reinforce the object structure.

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[267] BALDINI, Umberto – Teoría del restauro... p. 5.

[268] ICOM-CC - 15th Triennial Conference held in New Delhi in September 2008.

[269] *Idem*.

Restoration is a direct intervention on tangible cultural heritage, and this action is only performed whenever an artifact has seriously deteriorated, despite implying the object stability it can modify the artifact's appearance.

17.2. Ethical code and intervention criteriae

In the ambit of conservation treatments and restoration the approach methods adopted throughout the years have undergone important changes, which can also represent the latest intervention theories and culture, finally being important data for the history of the archeological artifact itself.

Considering this, we observe a growing interest together with a significant number of *statements, documents, letters and intervention basics*, not only in the sense of the heritage clarification notion but also to enlighten intervention strategies. These readings allow the comprehension of key changes in a few concepts, particularly the ones applicable to preventive conservation, progressively extinguishing a more invasive methodology.

In spite of the new definitions of conservation, the documental and historic value concern of the artifacts remains, together with the authenticity of preservation and the appeal of minimum intervention. However, despite the advantages they also present some disadvantages.

Based on the ethical code ruling conservation and restoration[270], basic fundamentals of intervention are referred to: i) reversibility, from which all intervention of restoration should be likely to be removed without damaging the original object; ii) compatibility, as all materials and techniques applied should not cause physical, chemical or mechanical damage to the original objects, with particular attention to aesthetics as well; iii) recognition, restoration actions should be distinguished from the original without losing the whole picture; iv) minimum intervention, as all conservative action should be self limited to the necessary minimum in order to preserve the safe, historical and artistic dignity of the studied objects. On the theoretical point of view and conciliating all these ideas, treatments should be limited, with minimized risks to heritage.

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[270] ECCO - European Confederation of Conservator-Restorers´ Organizations. Professional Guidelines.

However, this theoretical effort, developing a directed action towards archeological heritage in general and underwater in particular, is many times subjective. This situation is a result of the own essence of archeological artifacts, hence Cesare Brandi in his *restauro crítico* points out a series of obstacles and restrictions associated to the traces of the archeological character[271].

17.3. Reversibility, retreatment and minimum intervention

The amalgam which we are faced with towards an underwater archeological site can be decomposed through a scientific study capable of identifying decomposition and physical changes suffered. This analysis, will able an effective usage of the inherent resources of the conservation procedures, mainly the ones concerning non-intervening actions as preservation *in situ* or passive treatment, from which we aim to save cultural heritage without inhibiting future possible interventions. These measures can be considered as minimum intervention.

However, this option carries out some less good consequences such as accessibility inhibition and the impossibility of direct visualization of the objects, being only appreciated at the level of preventive conservation[272].

In spite of this situation the most problematic questions remain with the duality of some of the principles, namely their reversibility and authenticity.

The concept of reversibility comes from the theories of Cesare Brandi being promulgated by the *Carta de Restauro* (1972)[273]. This is linked to the idea that all added elements should be able of being removed at any moment, not causing damage to the original object[274]. However, considering the chemical characteristics of commonly used materials in conservation and restoration, such as synthetic organic polymers, acrylic polymers and co-polymers or natural polymers[275], it is possible to verify that none of these are able to be fully removed[276]. Therefore, the word reversibility should only be applied regarding the solubilization process and not for the description of a certain

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[271] BRANDI, Cesare – Theory of Restoration, I... p. 233.

[272] THOMSON, Garry – *Op. cit.* p. 130-156.

[273] MARTÍNEZ JUSTICIA, María José, trad. - Carta del Restauro 1972.

[274] FERNÁNDEZ ARENAS, José – Introducción a la conservación del património... p. 153.

[275] CHANG, Raymond – Química... p. 1089-1113.

[276] GIUSTI, Annamaria – Reversibility in the restoration... p. 91-93.

material[277]. Thus, since chemical materials introduction is inevitable in conservation treatments, and since it is impossible to remove all the chemicals introduced during conservation treatment, this means that the reversibility principle should not derail any treatments, even if it implies the use of a non-soluble chemical. The prime need is always to secure elemental components, as an irreversible treatment could mean long-time survival for fragile artifacts.

On the other hand, it is important to clarify that this concept arises along with the definition of work methodologies linked to paint restoration and then applied to other areas, without any consideration of the enormous difference between them. When talking about restoration and conservation of wet organic archeological materials, we are faced with a difficult situation about how to execute this concept. Even practices considered as the most peaceful ones, end up having repercussions which are not always accompanied by the recovery of the original form.

Although recognizing the importance of this concept, it is understood that we should not cease to accept the practice of some safeguard procedures with a less reversible focus, as otherwise this would result in total paralysis[278], which unquestionably would be even more harmful for the objects in question.

The thorough reading of the authenticity definition implies the recognition of distinctive components in defining the shape of the archeological artifact, as its material nature, its function and ideas of its origin, that is, all the factors that are part of its authenticity[279]. However, in numerous situations there might be a modification of those requirements, as a result of the components physical and chemical mutation. On the other hand, its functionality or meaning might have been the target of several changes. From this point of view, and when historical facts are appreciated, elements to be preserved are defined, preferably without harming other data.

When intervening in an underwater archeological object, we must realize that those actions cannot induce an incorrect identification[280] or a mystification of the original object. That said, a basic question must be placed: what are the limits of the intervention and what type of materials should be used. The answer might be in the

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[277] APPELBAUM, Barbara b) – Criteria for treatment... p. 65-73.

[278] MUÑOZ VIÑAS, Salvador – Teoria contemporânea de la Restauración... p. 115.

[279] APPELBAUM, Barbara a) – Conservation Treatment Methodology… p. 255-257

[280] Assuming that there is some difficulty distinguishing between two instances of the same type and considering that almost all elements are reproducible, it is noted that this type of situation can trigger a presentation of a false, regardless of the purpose for which was granted. ECO, Umberto – Os limites da interpretação… p. 181-217.

dialogue between different disciplines. Its authenticity cannot be judged only from the point of view of a conservative and restoration action but as a result of a multi-discipline character.

If the principles mentioned are subjective, the only idea that can be put into place without being misread is compatibility. According to this, it is understood that all materials incorporated in the original object should possess physical, chemical and aesthetic compatible properties and all of these together contribute towards to a harmonious aging process.

Still, although recognizing the importance of the concepts, it is important to take into account that these are guidelines that must be evaluated all together. To base the safekeeping of waterlogged organic archeological materials just on one principle would not bring any benefit; hence these elements often present a high complexity with a high degree of demanding treatments. In these cases, reversibility and minimum intervention are not truly achievable, and both present a great amount of limitations, without a guarantee of long term conservation, a general public access, or the improvement of aesthetic appearance.

Conservation of waterlogged archeological organic materials should allow balanced and appropriate solutions to each situation, supported by common principles of professional practice, but still in close relation with other disciplines such as archaeology and other areas.

18. Conservation procedures

Conservation measures and actions can have more than one purpose. For example, the on-site preservation measures can be considered as a preventive procedure but also as part of *in-situ* preservation or even as the first step of laboratory conservation.

Despite the possibility of having this in common, there are major differences between the *in-situ* preservation and the laboratory conservation procedures, which are related to the purposes, degree and techniques of intervention of each, but culminating in budget differences. The first intervention can be seen as not so costly storage, where decay rates are less accelerated, and as for laboratory conservation it implies stabilization treatments which will depend, basically, if the artifact is to be displayed or to be stored.

18.1. *In-situ* preservation and storage

In the course of excavation many kinds of organic materials can be discovered, with different nature, size and shape. According to the UNESCO Convention for the Protection of the Underwater Cultural Heritage, "the preservation *in-situ* of underwater cultural heritage shall be considered as the first option before allowing or engaging in any activities directed at this heritage"[281]. However, conservation in most cases determines that regarding organic materials only wood should be protected *in-situ*. The reasons for this different approach are the high costs, both in time and money, for the stabilization of a wreck or other wood structures and the importance of presenting cultural heritage in its *original* environment. Regarding other organic materials being so rare and fragile, and their decay so complex, a model for *in-situ* preservation or a reburial environment has yet to be established. Thus, *in-situ* preservation and storage arises only as a preventive measure, an option for long-term preservation of wooden structures.

To achieve a better understanding of the underwater environment and to improve *in-situ* preservation strategies, over the past twenty years studies and projects have been developed in wetlands, river floodplains, low lying urban sites and totally submerged sites, such as lakes or a marine environment[282].

The techniques that have been used are based on the recreation of the original burial conditions, providing a stable reburial environment, but still this methodology does not stop degradation of archaeological organic material, it only slows it down. According to investigations, marine borers, fungi and bacteria are present at the surface or in a shallow burial, causing the degradation of materials. Furthermore, in reburials 50 centimeters (cm) deep into the sediment, water and oxygen content decrease but

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[281] UNESCO - Convention on the Protection of the Underwater Cultural Heritage UNESCO Paris, 2 November 2001. Article 2.5.

[282] CURCI, Jessica - The Reburial of Waterlogged Archaeological Wood... p. 21-23.

degradation by anaerobic bacteria follows[283]. Therefore, in order to decrease the degradation rate, materials should be buried deeper than 50 cm.

However, it still is necessary to know the original environment, once the goal is to restore or to create the original burial context and also to predict the rate at which the different materials decompose. So it is crucial for the *in-situ* preservation to analyze first the environment of the site before any disturbance occurs. The collected information will also be needed for the choice of the type of protection for the site.

The study implies field experimental analyses, for which working with marine biologists, chemists or other specialists, is essential to obtain good results. The major parameters to be researched should include data on sediment dynamics and its vertical wall, phosphate[284], pH, redox potential (E_h), temperature, salinity, biological activity[285], the amount of dissolved oxygen and water level[286]. Other parameters that can be also measured include levels of sulfide, alkalinity, nitrate, ammonia[287], silicate and iron. A data logger placed *in-situ* can be used to collect data, or samples can be taken from sediment cores and analyzed in laboratories. For better results buried wood samples can also be employed in order to determine the decay rate[288].

This phase is followed by the re-burial of woods or wooden structures and with the data collected the environment is recreated. Because the natural equilibrium takes too long to form and before borer organisms attack it is necessary to artificially cover the materials or the site. At first, materials must be physical protected by placing a synthetic geotextile made of polyester and polypropylene[289] or a polymeric mantle, a net of polypropylene (50% density)[290] or even a black-shading net in polypropylene (40-60% density)[291] can be used.

These materials are chosen according to the need of each site or structure. The geotextile and polymeric matting are used to create a flexible physical barrier, due to their fibers characteristics water and finer particles are able to penetrate, protecting the

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[283] GREGORY, David a) – Re-burial of Ship Timbers... p. 82; BJÖRDAL, Charlotte G.; NILSSON, Thomas – Laboratory Reburial Experiments…

[284] MATTHIESEN, H. b) - Phosphate release from marine sediments...

[285] RICHARDS, Vicki; [*et al.*] – *Op. cit.*

[286] HOGAN, D. V.; [*et al.*] – *Op. cit.*

[287] GREGORY, David; MATTHIESEN, Henning; BJORDAL, Charlotte – *Op. cit.*

[288] KLAASSEN, René, ed. – *Op. cit.*

[289] POURNOU, Anastasia; JONES, A. Mark; MOSS, S. T. – In Situ Protection...

[290] MANDERS, M. R. – The In Situ Protection...

[291] MANDERS, M. R. [*et al.*] – The physical protection...

site and helping to retain particles. Nets serve to capture sand or sediment that penetrates in the holes and settles, creating an artificial mount.

To temporarily hold the geotextiles or nets, sand bags can be used until the deposition occurs. For a longer duration the chosen bag must be made of UV-stabilized polymeric fibers. Since natural deposition of sand or sediments can take a long time, a faster measure of covering must be taken, by using a water dredge and proceeding with the deposition of sand or sediments. All the area must be covered with a sand mantle higher than 50 cm and larger than the site itself[292].

When the reburial is finished, the work is still not complete as many situations can occur after *in-situ* preservation measures or storage have been done, the most common being: tidal and current forces that move sand or sediments, exposing the structures and producing mechanical and morphological consequences, or chemical transformations. Since it is very difficult to predict how the environment will change, underwater reburied sites must be verified. Therefore to achieve successful preservation, monitoring and maintenance of the burial environments is essential.

A monitory strategy can be done through: i) data loggers; ii) installation of piezometers (dipwell) or lysimeters; iii) burial of softwood and hardwood blocks; iv) periodic inspections. The data loggers will serve to analyze chemical aspect such as, pH, E_h and oxygen content. As for the piezometers and lysimeters, the first quickly detect changes in a long or intermittent period[293], and the second can be used to understand the periods and decay stages within two years[294]. The information given by both devices will act as a representation of the environmental conditions, whereby they should be used in conjunction with other methods of analysis. The burial of woodblocks will serve as controls to understand which processes are responsible for the deterioration in various stratigraphics, beginning just below the sediment until 50cm deep, and in periods of three, six and twelve months, according to which must be collected for laboratory examination. Lastly, the periodic inspections, in which it is possible to verify if the site is totally and proper covered with sand or sediments and also to collect sediment samples to be examined in a chemical laboratory.

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[292] Several techniques have been applied for the reburial of underwater archaeological sites and over the years better measures have been developed. For an example of some of the techniques and their results see RICHARDS, Vicky; [*et al.*] – *Op. cit.*

[293] DAVIS, M. - In-situ monitoring...

[294] LILLIE, Malcom; SMITH, Robert – The in situ preservation of archaeological remains... p. 1494-1495.

Another feature of *in-situ* preservation is the storage of waterlogged organic materials in wetlands or near the coast. The concept of this procedure is based on the characteristics presented by a non-archaeological waterlogged area and materials needs. As a result, reburial of finds is made in a new and separate place that must have excellent preservation conditions.

Like *in-situ* preservation, two steps of investigation are required for *in-situ* storage: the data on the chosen burial area and after the burial of materials the monitoring of the site[295]. The first step is important to collect information on the physical, chemical, biological, hydrological dynamics and stratigraphy of the selected site. If the chosen area is a wetland, due to its variations and unique nature, microbiological properties and carbon retention levels have also to be considered. For the second step, it is essential to monitor the oxidation-reduction, the pH, the water levels, the dissolved oxygen content, temperature, microbiological activity and study the organic matter decomposition rates, by burying at different depths woodblocks that must be collected according to a certain period of time and analyzed. As well as *in-situ* preservation the best way to perform such survey is using piezometers, lysimeters and data loggers.

Worldwide results obtained from these methods of preservation have revealed that they are quite effective rather than other conservation measures, but the need to monitor, to collect data and to proceed with laboratorial analyses makes these techniques still quite expensive.

In Portugal, long-term storage of waterlogged wood has been being developed since 2003, with the finds recovered from the River Arade. Due to all the centuries of human occupation in that region and maritime activity from Silves until the Atlantic Ocean, the River Arade possessed a great quantity of archaeological artifacts. To better complement the Portuguese Underwater Heritage Archaeological Find Chart a project was developed, the *ProArade*, which included the excavation of the east area of the river, where a shipwreck was discovered. During this excavation, wood, ropes, metal and pottery were found[296]. After the archaeological research and given the large amount of materials lifted, two options were considered: to keep them in tanks with fresh water and perform a preservation laboratorial treatment, or bury them in a predetermined

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[295] HOGAN, D. V.; [*et al.*] – *Op. cit.*

[296] RAMBELLI, Gilson; CALIPPO, Flávio Rizzi; BAVA DE CAMARGO, Paulo F. – Relatório Participação Brasileira...

location. Due to the costs of the first option, the second was chosen by the direction of CNANS. The burial area chosen was located in the River Arade and it presented a good access for divers, as well as tides and currents protection. The artifacts were identified, flagged, wrapped in shading net and buried. After one year, this storage area was inspected by a professional diver from CNANS that verify if the materials were totally covered with sediment.

Two main situations must be pointed out: there was not an investigation into the nature of sediment or the chemical characteristics of the burial site and there was not an effective monitoring program, therefore any results or data were associated to the preservation of the buried materials. Hence the possibility of the River Arade being a good location for *in-situ* storage is still not known.

From the studies of marine biology it is possible to recognize seasonal changes in pH, Eh, dynamics of the sediments, salinity, water temperature, tides and currents and growing of marine life.

To consider this river or other area as storage, further research work is needed and protocols for monitoring the decomposition of buried organic finds have to be developed. Training programs to improve archaeological divers how to work and collect samples are also recommended.

18.2. Pre-Lab measures

Not all artifacts are preserved or stored *in-situ*. A few may be chosen to be conserved on a laboratory where preservation treatments are developed. In general, this stabilization is done by a conservator, who begins by examining the artifact and establishing the procedures. Each object will require a specific treatment that will depend on the artifact's nature, its state of preservation and what is intended for it, meaning if the artifact is for display or if it is for storage.

Since the materials are lifted and treated on-site, they continue to be wet or damp. If it is decided to send them to a laboratory for conservation they must be protected against environmental atmospheric changes, which mean that the packing, apart from having to provide physical support, has to protect materials from drying, which can happen during transportation.

Before packaging the materials, unless they are in a very fragile state, they must be rinsed in clear water and wrapped in polyester film or in synthetic textile fabrics soaked in water. This will serve to keep the water content stable during transportation.

Waterlogged wood materials are usually heavy, due to the water content, but soft and fragile, due to chemical and biological degradation processes. In order to avoid physical damage it is necessary to prepare polyethylene foam cushions, plastic bubble pack in which finds are placed. When transporting several finds at the same time, these cushions can also be applied around the artifacts to prevent them being damaged by contact with others. It is also possible to make crates, of suitable material to carry from the on-site to the laboratory, filled with polyurethane foam[297].

For friable or small artifacts, if they are in tanks or containers immersed in water, they should be kept that way and transported in them. With this technique, handling is avoided. In this procedure the most important point is to verify that during transportation, objects do not move in the containers, placing padding around them if there is any leakage, that they are sealed and the lids well positioned. Other techniques can be used for these items if they are small: they can be individually wrapped but packed all together in the same container, or if artifacts do not have any salts they can be lyophilized.

After all these measures have been taken, legible labels are put on the package identifying the content, and conventional sign handling instructions and summary documentation are given to the person chosen to escort the artifacts. This documentation should include information about the route, set time-schedules, stops to be done to verify the conditions, to soak materials if needed and how to proceed when arriving at the laboratory. For example, information about how to remove the artifacts from the crates or containers, or which should be the first artifact to be removed from the transport vehicle and how it should be done.

Prior to any transportation, laboratories have to be prepared to receive the waterlogged organic materials, either with tanks, hydraulic arms systems, engines or any other transport system capable of lifting and moving heavy artifacts, with chemical products, materials and other supplies needed to perform treatments.

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[297] LESKARD, M. – The packing and transportation... p. 118-119.

18.3. Analytical techniques

As previously stated, the first step for the conservation treatment of wet organic materials is to examine artifacts according to their nature, production techniques and degradation phenomena. This will help to identify priorities among objects, develop conservation procedures and provide proper exhibition conditions and storage. Besides the information given by basic information techniques, major understanding of an artifact can be achieved through the use of analytical techniques.

Due to scientific developments and modern technologies the use of analytical techniques, in conservation science, has expanded in the past years, providing a better understanding of the origins of an object, its elemental composition, determining deterioration processes and improving the preservation of cultural heritage[298].

The analytical techniques used for cultural heritage research and conservation can be divided into invasive and non-invasive techniques, destructive and non-destructive analysis[299]. They are distinguished according to the impact that they have on the artifacts, thus, "invasive stands for the analyses that require sampling, producing some alteration to the object, while non-invasive stands for analyses that do not require sampling (…). Destructive presumes the alteration/consuming of a sample during its preparation and/or analysis. Non-destructive means that sample does not suffer any kind of preparation and that is not consumed or changed during analysis."[300]

Furthermore, these analyses can be classified according to the laboratory technique used and its interaction with the matter, or referred according to the information that they provide.

The analytical techniques used are based on light examination and microscopy, molecular spectroscopy, atomic spectroscopy, X-ray, mass spectroscopy, chromatography, thermal and mechanical analysis or nuclear methods. Due to the high range of tests and each one providing specific results, it is advisable to use a combination of tests to achieve wider information.

In underwater archeology conservation the most used analytical techniques are non-destructive, such as light examination by ultraviolet (UV) rays and X-rays.

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[298] STUART, Barbara H. – Analytical Techniques... p. 1-2.

[299] GÓMEZ GONZÁLEZ, Maria Luisa – La restauración...

[300] CORREIA, Andreia Sofia – Henrique Pousão's Oil Paintings… *Op. cit.* p. 23.

UV radiation is especially used in composite artifacts, since certain molecular structures absorb UV radiation and re-emit this energy as visible light, allowing different materials to be distinguished[301].

As for X-rays, since their wavelength is shorter and more energetic than UV radiation they are able to penetrate denser materials than UV, giving more accurate information[302] (Fig.17). There are other techniques that also use X-rays, for example, the X-ray diffraction (XRD) which reveals chemical compounds and computerized axial tomography (CAT) with which is possible to analyze different densities between materials composition and physical properties[303].

Destructives techniques can also be applied, like the scanning electron microscopy (SEM). This technique, which can be performed with wet samples, allows identification of elemental composition and its deterioration degree. More precise information can be given by SEM when combined with energy dispersive X-ray spectroscopy (EDS) which allows elemental and chemical data.

In some particular cases there are references to the use of other techniques, such as molecular spectroscopy, like Raman spectroscopy and nuclear magnetic resonance spectroscopy (NMR Spectroscopy). Raman was used for the identification of protein composition, components characterization, differentiation of materials and identification of deterioration degree[304]. As for NMR Spectroscopy it was used in wood from shipwrecks, like the Batavia, and other wooden objects and it allowed identification of its molecular structure, material degradation and the monitoring of the effects of conservation treatments[305].

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[301] STUART, Barbara H. – Analytical Techniques... p. 72-76.

[302] POLLARD, M. [*et al.*] – Analytical Chemistry in Archaeology... p. 93-101.

[303] GODFREY, I.; [*et al.*] b) – *Op. cit.* p. 34-35.

[304] STUART, Barbara H. – Analytical Techniques... p. 153-154.

[305] *Idem*, p. 175-176.

Figure 17 – X-Ray image of object number 7 from Faro A shipwreck. The X-ray image clarifies information about the length of the organic cable inside the concretion. Hospital de Faro, Imagiologia.

Conservation science ostensibly benefits cultural heritage research, contributing to the effectiveness of treatments and the dissemination of results. Since this is such specialized research work, in order to perform these analyses archaeologists and conservators have to have support from different expertise such as chemists, biologists, material science engineers or other specialists. This also implies major laboratory equipment which can be found in research institutes, medical centers, universities, and conservation and museum laboratories.

In Portugal, many of the analytical techniques described above are becoming easier to access through collaboration with universities and research organizations. Some of these institutions are the *Laboratório de Física, Química e Raios X* (*LFQRx*), *Instituto Politécnico de Tomar*, the *Laboratório HERCULES - Herança Cultural, Estudos e Salvaguarda*, *Universidade de Évora*, the *Instituto Tecnológico e Nuclear*, *Instituto Superior Técnico*, *Universidade Técnica de Lisboa*, and the *Laboratório de*

Conservação e Restauro José de Figueiredo (*LCRJF*), *Instituto dos Museus e da Conservação*, which have been recognized for the research carried out on cultural heritage.

19. Laboratory conservation treatments

The main purpose of conservation is to preserve the artifacts, which means to preserve their appearance, dimensions, flexibility and internal microscopic structure. Hence the first treatment to be considered is cleaning, followed by removal of sea salts from the objects and finally the removal of sulfides and iron oxides (FeO), especially in the case of wooden materials.

In all the preservation situations it is required to develop a process of drying that does not induce the collapse or shrinkage of the organic material structure. The moisture content in cell walls is particularly important, as when water leaves the cell wall the strain of it makes the interior of the cell walls collapse[306]. Because wood is not dimensionally stable, if waterlogged archaeological wood is allowed to dry (without any conservation treatment), fissures, distortions and cracks can suddenly happen and the mechanical strength of the structure wood is lost. Usually these anomalies are the result of dimensional changes such as collapse and shrinkage.

Collapse happens when water is above FSP; it results from the evaporation of water from the micro-fibrils and lumina of the cell walls. When the water leaves the cell, the surface tension forces the interior of the cell to decompress, generating a strong attractive strength that does not allow air to pass into the cell to replace water (capillary tension). The pressure inside the cell will be so powerful that it will lead to the buckling of it[307].

Shrinkage comes about as soon as the wood begins to dry, and once it happens it is difficult for wood to return to its previous size and shape, even if immersed in water. In this case, the changes begin when waterlogged wood is below FSP and water evaporates from the amorphous regions of the cell wall, making the existing space in the

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[306] WALKER, John C. F. **-** Primary Wood Processing... p. 69-94.

[307] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke. – *Op.cit*…p. 31.

capillaries decrease, thus a new (micro) fibrillar arrangement which leads to physical degradation[308].

The amount of shrinkage upon drying in archaeological waterlogged wood is correlated with the rate of wood degradation and the amount of water present, but is also related with the different direction. Hence, the bigger shrinkage rate is in the tangential direction to the annual growing rings, whereas, radially is less than the tangential and even smaller in longitudinal direction[309].

Over the last decades several conservation treatments have been enhanced, but all with the same guidelines: impregnation of the organic materials with a water substitute, chemically inert, that will act as a consolidant, which at the same time is able to lend mechanical strength to the materials[310]. Other treatments involving controlled slow drying, replacement of water for a non-aqueous solvent, and lyophilization or supercritical drying are also used.

All the steps given for preservation must be well documented, with laboratorial analysis included, as this will able conservators, curators and archaeologists to understand the current state of preservation of the artifacts, the preventive needs if any and if there is a need to perform a re-treatment or how to reverse the original treatments or how to develop a treatment compatible with the first one. All this information must be kept in the Object Sheet Report, which should include: i) the inventory number that can be used also as a laboratory number, and the number of pieces belonging to each artifact; ii) the registration date; iii) its provenance; iv) a full description of the artifact and dimensions; v) the nature of the material, its construction and appearance; vi) objectives; vii) proposed intervention; viii) procedures carried out; ix) photographs, for identification of the artifact and registration of degradation; x) the literature consulted; xi) analytical techniques performed.

Generally, documentation, impregnation, drying and data from analytical research are the most important steps in the conservation of wet organic artifacts, but do not mean that other treatments are not required. In fact, these will permit the success of the conservation intervention.

Regarding the development of any preservation procedure, facilities have to be prepared with two different areas, one for wet treatments such as cleaning, salt removal,

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[308] GRATTAN, D. W. b) – Waterlogged wood. p. 59-63

[309] GRATTAN, David b) – Wood Deterioration, Wood drying…p. 19.

[310] GRATTAN, D. W.; CLARKE, R. – Conservation of waterlogged wood... p. 165-166.

impregnation and bulking[311] and another for dry treatments of dehydration, deep cleaning and coating. Both areas will need to have[312]: tanks (made of plastic, tiles or metal lined in plastic) and plastic containers; trays; sinks; shelf storage; tap water, distilled and deionized water (produced by condensing steam water or by filtering tap water through a cartridge mechanism); solvent, acid and bases storage; ventilation; several hand tools, according to the work to be carried out; heater and refrigerator; stirring devices and circulator mechanisms; scales and other measuring devices; and magnifying instruments, such as lenses and microscopes.

19.1. Cleaning

After documentation and analyses have been done, the next step is the elimination of sediments, mud, silt, dirt and stains. In this process several methods can be used. Besides removing all external elements, cleaning also helps to reveal details of use and production.

In this operation materials must remain wet during the process. This will avoid collapse caused by drying. For this procedure, a table can be done with the different methods applied and their results. Another important aspect is to always perform a systematic cleaning of the entire artifact. Too much cleaning on just one side is not a good option as there are no certainties about how the rest of the object will react, i.e. aesthetic features have also to be present.

Since it is a procedure that cannot be reversed it can be harmful for artifacts, so archaeologist and conservator must begin with a series of tests, from the least to the most interventional[313].

Cleaning is usually divided according to the methods used: mechanical or chemical. In the mechanical process, the artifact is not just released from dirt, if sediment was brought to serve as an additional protective element that sustains the object together, it will be needed to perform a micro-excavation. In the course of this

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[311] These treatments prevent cell wall shrinkage, by enter into the molecular structure and replacing water (nonreactive treatments) or bond with the cell wall (reactive treatments), thus the cell wall is strengthened and more resistant to collapse. However, they also change cell walls' mechanical properties. BARBOUR, R. James - Treatments for Waterlogged... p. 186.

[312] This list is just a summary, refers only to elements and equipments most commonly used, however, others may be necessary.

[313] CAPLE, Chris – Conservation Skills... p. 99-100.

procedure instruments such as scalpels, needles, dental picks, several kinds of brushes, wooden tools, such as toothpicks and spatulas, a range of probes, electric instruments such as air compressors for blowing the surface of the artifact, vacuum cleaners, engravers with different pointers to remove concretions, will be needed. These are the most used ones but other instruments can be helpful, as long as they do not damage the surface of the organic archaeological objects.

Regarding chemical cleaning it serves to remove dirt, stains, oils or odors. In this process reagents have to be added as they work through changing the molecular composition of dirt, making its insoluble constituents into soluble ones.

This process includes the use of water at different pressures, sprayed or atomized; dissolution agents, solvents, heat or energy. A good dissolution agent can be a detergent used at 5%, with a neutral pH and after washing, rinsing with distilled water. Due to its molecular properties (one part is polar and the other non polar) it will bind with water and with the organic matter from dirt or sediments allowing its dissolution, thus its removal.

Whenever using water to clean an artifact seems to be very destructive, organic solvents (such as acetone, methyl acetate, ethyl acetate, hexane, petrol ether or ethanol) may be used to remove dirt from surfaces instead. As for heat or energy, these methods are only applied to objects that resist this type of approach.

There are several chemicals that can be used to remove stains; the choice of chemical product will depend on the type of stain. Black stains from sulfides are produced by bacteria and mold, orange from iron, blue or green from copper. Usually for the biological stains a solution of 3% to 10% of hydrogen peroxide (H_2O_2) in deionized water can be used[314]. This chemical acts like bleach, so the washing solution cannot be performed for hours. Also, the rinsing has to be done carefully and several times with distilled water.

Metallic stains can be removed through a chelating agent[315] such as ethylenediaminetetraacetic acid (EDTA) ($C_{10}H_{16}N_2O_8$), in a 5% solution, or by a solution of 2-5% ammonium citrate ($Nh_4)_2HC_6H_6O_7$) or using hydrochloric (HCl), hydrofluoric (HF), citric ($C_6H_8O_7$), formic (HCOOH), acetic (CH_3COOH) or oxalic ($H_2C_2O_4$) acids, all used in an range of solutions between 2% to 10%, depending on the

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[314] RODGERS, Bradley R. – *Op. cit.* p. 45.

[315] Also called chelants, chelators, chelating agents, or sequestering agents. It is a chemical compound formed by a metal ion attached by covalent bonds to a number of hetero-organic compounds, which inactivates the other metal ions producing its precipitation.

nature of materials (see next subchapter). These treatments can take several days or weeks to complete and must be controlled every day.

Usually, chemical methods imply a change in pH according to the reagent use, acid, basic or a salt. These chemicals have to be completely removed otherwise they will continue to act, degrading the materials. This procedure has to be performed after each cleaning session. Its neutralization requires the introduction of a reagent in another range of the one used, i.e. if the used product is a base, an acid has to be added. Another good measure is to rinse the object several times with water, as this will dissolve the reagent.

After cleaning, the artifacts can be placed in bags or containers filled with water and, if possible, refrigerated to reduce the potential of biological growth.

Although cleaning is not a simple task, since some decisions have to be taken especially on how to do the cleaning and when to stop it, if the treatment is carried out with sensitivity and common sense it can be performed either by archaeologists or archaeology technicians.

19.1.1. Leather, bone, antler, teeth and ivory

Most leather appears to have the grain side fairly dirty and the weak flesh side cleaner. Despite this difference, both sides can be cleaned in running water using soft brushes to dislodge dirt and external particles matter. As for hard corrosion deposits and concretions they can be removed from a leather surface using different type of wooden and plastic tools or ultrasonic dental equipment.

To remove oils, fats, strong odor or iron stains a chemical cleaning has to be done. The anionic surfactant sodium lauryl sulfate ($CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOSO_3Na$) or a non-ionic detergent can be used in an aqueous solution at a very low concentration to clean oils, fat and even dirt or soiling[316].

For odor, sodium bicarbonate in a slightly alkaline solution works very well. This method involves a solution of 2% (w/v) sodium bicarbonate and the introduction of the piece in this solution for 30 minutes, followed by repeated rinsing, and washing with

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[316] KITE, Marion; THOMSON, Roy; ANGUS, Aline - Materials and techniques... p. 125.

a 0.5% (w/v) solution of sodium lauryl sulfate for 30 minutes to 1 hour, followed by significant rinsing[317].

The removal of iron stains implies choosing from several chemical solutions, the most used being dibasic ammonium citrate solution (or ammonium hydrogen citrate, $(Nh_4)_2HC_6H_5O_7$), the EDTA and the sodium dithionite solution (SDT) (also known as sodium hydrosulfite and sodium sulfoxylate, $(Na_2S_2O_4)$.

Dibasic ammonium citrate is a slow and gentle chelating agent used in aqueous solutions of 2-5% (w/v) with a pH of 5.3. Treatment progress has to be judged based on the color of the solution: the darker the solution, the more time the objects have to be in this solution, after which heavy rising has to be done.

Another chelating agent is also EDTA, it forms soluble complexes with metal ions, it presents a pH of 4.5 and it has been used for leather in 2% a 5% (w/v) solutions in immersion with a range 4 to 36 hours, with rinsing times from days to weeks, respectively.

SDT is a water-soluble salt reducing agent with a pH of 6-7 and a weak sulfurous odor. It reduces corrosion products to a more soluble form, allowing other chelating agents to act. Although it is stable under most conditions, it is important to work as quickly as possible, since it reacts with water and dissolved oxygen increasing the solution acidity. This is also the reason to never use hot water and acid solutions. After treatment, thorough washing is required. This way, the new soluble ions (Fe II) are removed. If this procedure is not done well the stain will return, since the remaining ions (Fe II) will oxidise once again.

The Canadian Conservation Institute (CCI) developed a treatment to remove iron stains from leather and leather related materials. This method uses a 5% (w/v) of SDT combined with a 2% (w/v) of EDTA, followed by rinsing[318]; the results were most effective and less time consuming.

Since treatments to remove iron stains can also lead to the removal of dermal impressions, surface effects[319], tannins, dyes and also hydrolyze collagen, any method chosen has to be carefully considered.

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[317] GRANT, Tara; Cook, Cliff; Binnie, Nancy – Archaeological Conservation…p. 7.

[318] LAFRANCE, Jessica - Efficiency and quality in a bath treatment …

[319] GRIEVE, S. - Leather Shoes from the Civil War...

Due to the fact that leather can be very fragile, during the cleaning process leather pieces can be placed in a tray covered with nylon net, secured with clamps, and then soaked with water or with a cleaning solution.

The cleaning of bones, antler and ivory is easy for archeologists, restorers or archaeology technicians to accomplish, however it may result in the lost of information needed for archaeological research, therefore when performing this operation, constant care must be taken.

Mechanical cleaning can be achieved by simply using a gentle flow of running water and a soft brush, even when dirt is more attached, no metal tools should be used, but a swab to dislodge the dirt particles. Due to the soft surface of bones this cleaning must be gentle.

A 5% (w/v) sodium dithionite, or 2% (w/v) dibasic ammonium citrate or a 5% (w/v) EDTA solution can also be used on these materials for removal of stains. These treatments can be performed until 6 weeks, changed weekly in the case of ivory and after 4 weeks for bones. In both cases, rinsing with water must always be done after treatment[320]. Other solutions using acids can be used to remove iron stains, such as a 5-10% (w/v) oxalic acid (HO_2CCO_2H), or a 5% (w/v) ammonium citrate followed by 5% (w/v) oxalic acid[321]. When the removal of stains is complete, to neutralize the acid used a one-hour rinse with 1-2% (w/v) sodium bicarbonate solution is necessary.

Chemical cleaning may reduce the mass or decompose the calcium carbonate and cause structural stress in the artifacts, thus, these treatments cannot be performed on deteriorated artifacts. For fragile bone, teeth or ivory, treatment must be through localized applications of one of the chemical solutions presented, which are neutralized using a swab with water.

For sulfide stains, a 5-10% (w/v) hydrogen peroxide can be used, or a sodium hydrosulfite solution, followed by diluted hydrogen peroxide to remove any remaining stain[322].

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[320] GRANT, Tara; Cook, Cliff; Binnie, Nancy – *Op. cit.*

[321] HAMILTON, Donny L. a) – *Op. cit.* p. 17.

[322] *Idem*, p. 17.

19.1.2. Fur, wool, hair, horn and tortoiseshell

For keratin materials, due to their susceptibility handling must be avoided, hence treatments must be performed on an individual basis and as quickly as possible, avoiding long rinsing times, which may cause further delamination. First the materials must be placed on a polyethylene net frame, then running deionized water, a soft brush and a non-ionic neutral detergent or sodium lauryl sulfate at 0.5% (w/v), can be used to remove all dirt.

19.1.3. Silk

Like collagen and keratin materials, silk must always be cleaned using a synthetic net frame support. If silk is in a good state of preservation, deionized water added with a non-ionic detergent, or a disinfectant in a concentration of up to 0.1%[323] can be used along with sweeping with a soft brush. If the material presents a fragile condition, cleaning must be done only by running deionized water, with no addition of surface-active agents.

Usually silk presents several stains[324] which is due to the addition of mineral salts and metals used to give more weight and a stiffer texture to silk. As the rate of deterioration increases it promotes the emergence of metal stains and since these substances and silk are so different, complex treatments have to be developed. In these cases EDTA solutions have to be avoided because they appeared to be the most detrimental towards silk[325].

Furthermore, silk has metal threads meaning that it is affected by the cleaning methods used for these threads. In these cases the best way is to use a non-ionic detergent in softened water[326] and after the stabilization and study of the metal, perform the cleaning of the metal through cotton swabs with an appropriate solution.

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[323] PERJÉ, Judit B.; NAGY, Katalin E.; TÓTH, Márta – Conservation of silk finds... p. 2.

[324] TIMÁR-BALÁZSY, Ágnes; MATEFY, Gyork; CSANYI, Sandor - Effect of Stains and Stain..

[325] JOHANSEN, Katia – Assessing the risk of wet cleaning...

[326] Water that does not present a concentration of calcium, magnesium or other ions.

19.1.4. Cellulosic materials – textiles, rope and wood

The differences between cellulosic materials lead to distinct cleaning methodology.

Due to its fragile nature, textiles or rope must always be supported on a synthetic net structure, in which they are washed, unfolded and fully spread out, preventing rupture at the fold line. The cleaning implies a solution of deionized water and 0.5%-1% (w-v) of neutral non-ionic detergent[327] or 1% of ammonium hydroxide (NH_4OH). During this operation great care has to be taken with dyes, and to prevent the possible fading of pigments and dyes, pH has to be controlled to a neutral point.

If the material appears to be in a good state of preservation but stained, removal solutions can be applied, such as being soaked in deionized water at 38ºC with a nonionic detergent, for 15 minutes[328], immersion for 30 minutes to 1 hour in a solution such as 4% (w/v) hydrogen peroxide with 4% ammonia, or a solution of 1L of deionized water, with 60 ml of 30% (w/v) hydrogen peroxide, with 2.5g sodium silicate (Na_2SiO_3) dissolved in 100 ml of hot water, or even a solution of 1L deionized water with 300 ml of 30% (w/v) hydrogen peroxide, with 20g sodium silicate, 5g sodium carbonate (Na_2Co_3) and 5g sodium hydroxide (NaOH)[329].

Metal corrosion products cause visible and unaesthetic stains that generate structural damage and bulk the fibers. For its removal an aqueous solution of 5% (w/v) of oxalic acid is quite effective for the elimination of iron encrustations, especially if cleaning in a short period of time is needed (1 or 2 days)[330]. Others solutions can be used such as 5% (w/v) hydrochloric acid, 10% hydrofluoric acid (HF), 5% EDTA, disodium, 5% acetic acid (CH_3COOH), 5% formic acid (HCOOH), or 2%-10% ammonium citrate [$(NH_4)2C_6H_6O_7)$][331].

Due to the cotton textiles sensitivity to a lower pH, the presented solutions are not recommended for these types of fibers, or if used they must be very well monitored, hence they have the highest pH of 2.5 (hydrofluoric acid) and the lower pH of 0.7 (hydrochloric acid), thus they can be very damaging for these fibers[332].

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[327] JENSSEN, V. - Conservation of Wet Organic Artifacts...

[328] TARLETON, Kathryn S.; ORDONEZ, Margaret T. - Stabilization Methods for Textiles... p. 85.

[329] HAMILTON, Donny L. a) – *Op. cit.* p. 38.

[330] MORRIS, Kenneth; SEIFERT, Betty L. – Works Conservation of leather and textiles... p. 38

[331] HAMILTON, Donny L. a) – *Op. cit.* p. 39.

[332] *Idem*, p. 39.

For hemp, jute and bast fibers the best results can be achieved with an aqueous solution of 2% (w/v) triammonium citrate ($C_6H_{17}N_3\ O_7$), with 5% (w/v) sodium dithionite ($Na_2S_2O_4$)[333].

After the stain removal process is complete a final rinse in deionized water must be done. This rinse can take several hours until a neutral pH is achieved, meaning that the water should be changed according to the pH measures taken.

During these procedures handling of the textiles and disturbing the water must be avoided, since movements may damage the fabrics. Also, after each session the materials must be placed in a net support and then into the refrigerator or container.

Waterlogged wood usually has a dark surface, from the metallic salts and/or from the sulfide staining from organic substances present in the anaerobic environment, and a very soft and spongy surface covered by extraneous materials, such as mud, silt, concretions, barnacles and shells from biological attack. Both situations need to be removed since they block the penetration of consolidants and also mystify the original appearance of wood materials.

The first cleaning operation should be the removal of all extraneous materials. This is accomplished by a gentle cleaning with running water, sponges and soft brushes. For more strongly attached extraneous materials they can be eliminated by mechanical cleaning using pliers, forceps, dental picks, scalpels, mini crafts or pneumatic air scribe devices.

Given the fragility of waterlogged wood, during this process, degradation of the surface can take place, along with distortions, fissures and cracks. Such a situation is due to the physical strength upon the materials, but also because of the capillary tension collapse that occurs, even when cleaning is done without drying the materials.

Similar to other cellulosic materials, metal stains in waterlogged wood can block other treatments like bulking and impregnation, needed for the stabilization of wooden materials, thus a chemical cleaning with acids or sequestering agents has to be done.

For removal of metallic stains citric, oxalic, or hydrofluoric acids can be used in concentrations of 3%-10% (w/v). Since acids break down the wood on a cellular level general soaking is not recommended, which means that for this treatment cellulose pulp or cotton-balls, impregnated with the chosen chemical, must be punctually applied upon the stain.

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[333] GODFREY, Ian; KASI, Kalle; RICHARDS, Vicki – *Op. cit.*

To remove organic stains a 3%-10% (w/v) of hydrogen peroxide solution can be used. Again the patch method has to be used. The removal of stains can take several minutes or days: until the treatment is complete the patches will need to be changed, and during changes a more dilute solution can be applied[334].

If the chemical solution used is not removed, it will have harmful effects on these materials, so after the removal of stains the area must be rinsed with deionized water.

During cleaning sessions, waterlogged wood should be stored in tanks with water circulation. This will help to reduce biological activity, which usually appears on the wood surface as slime. The appearance of slime also indicates that the wood is still continuing to deteriorate even in storage.

Another option to prevent fungi, bacteria and algae growth is the use of chemical biocides. However, this alternative represents a health hazard[335], and the chemical product chosen cannot enable C14 dating, other investigations or future preservation treatments.

19.2. Desalination

As a result of a long-term exposure to a water environment, organic waterlogged artifacts usually contain a large amount of chlorides and other soluble and insoluble salts. Soluble salts can be dissolved, through a process in which a large amount of ions will be diffused into the solution. On the other hand, the insoluble or poorly soluble salts, are those where just a small amount of ions get diffused into water.

Salts are particularly harmful as if the artifacts dry they will crystallize and expand, damaging the structure. In order to prevent artifacts being damaged the salts must be removed. This is achieved by introducing the objects in fresh, deionized or purified (by reverse-osmosis, RO) water. If an object is from a marine site, which typically presents a considerable salt concentration in the cells, the introduction into water must consider the use of sea-water diluted with tap water and the progressive mixing of waters (first 75%-25%, followed by 50%-50% and 25%-75% sea-water and

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[334] KAYE, Barry; COLE-HAMILTON, David J. – Conservation of knife…

[335] MOUZOURAS, Renos - Micro-organisms-mechanisms…

fresh water) providing the adaption of the cell structure to a new osmotic pressure, preventing its collapse.

The water must be changed gradually, each time equilibrium is reached, until only RO water is used. The amount of water or water solutions used must be sufficient to cover all the objects, plus several liters.

Through these successive baths, the soluble salts are progressively reduced since they move out of the artifacts into the water. However, it is not possible to predict the amount of time needed to carry out desalination, as even if materials are from the same site they can present differences between them and so the desalination will differ. To know the amount of salts that are removed from the objects, the solution needs to be monitored and recorded on a weekly bases. This can be done by taking samples from the various desalination baths and measuring their conductivity. This information will also help to evaluate when the salt levels rise in a solution, meaning that the water needs to be changed, in order to continue the diffusion of the salts. To measure the quantity of salts a conductivity meter is suggested, rather than a chloride meter, since a number of types of salts may be present in the object and chloride meters only measure effectively the removal of chlorides. Also a conductivity meter is less expensive, portable, easy to use and does not need to be calibrated as often.

At this stage the amount of water consumption can be very expensive but several strategies can be developed such as the use of rain water or the reuse of solutions, by placing a pump that will carry less salty solutions to other tanks, replacing the ones that are more salty. This pump will also serve to daily move (moderately) the water, reducing the concentration of salts around the object, increasing the efficiency of the salts removal.

Despite the positive effects of the salts elimination, the changing of environment also has to be considered as a situation that can cause the deterioration of materials, since equilibrium has to be reestablished each time the water is changed.

19.3. Conservation treatments for waterlogged organic materials

A key part of the conservation of waterlogged organic materials is the stabilization of the artifacts, while maintaining their dimensions and saving most of the surface details (gilding, dyes, paints and notch). There are different methodologies for the stabilization of organic materials, the most usual are: the replacement of water with an impregnation or a bulking material; the substitution of water by a solvent, followed, or not, by the introduction of a bulking agent; freeze-drying; a combination of all these techniques; or supercritical drying. Despite the several treatment choices, the criteria of treatment mainly depend on the nature of each material, its preservation state and size.

19.3.1. Polyethylene glycol impregnation

One of the approaches that involve impregnation and bulking is the use of polyoxy1-2ethanediyl, i.e., polyethylene glycol (PEG) [$HO-(CH_2CH_2O)_n-H$]. This method, first synthesized in 1859, but only introduced in conservation in the 1960's[336], is more often used to replace water in the wood structure but it can be applied to other materials.

PEG is presented with different molecular weights, viscosity (the higher the molecular weight, the higher is the viscosity), surface tension, freezing, melting points and different solubility with different solvents, thereby allowing different treatment approaches. The reason for these characteristics relies on the chemical compounds, the hydrogen bonds and their ability to link with water molecules, through the oxygen atoms. It is also these hydrogen bonds that will act as a support for the waterlogged wood.

For conservation of waterlogged organic materials, especially wood, PEG is used in molecular weights between 400 and 4000 g/mol ($n = 9$ to 91). Water is added to this chemical and materials are impregnated with this aqueous solution of PEG. The impregnation can be done by submerging[337] or by spraying the artifacts[338] with the chosen PEG solution.

Typically, the impregnation begins with a solution of a low percentage of PEG with low molecular weight (from PEG 200 up to PEG 400), which penetrates the cell wall, micro capillaries and the fibrils, followed by a solution of a high molecular PEG (PEG 3350) that will fill the lumen and pit membranes[339]. In deteriorated wood the

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[336] Christensen, B. Brorson – *Op. Cit.*

[337] The conservation of Skuldelev ships are a good example of the impregnation by submersion with PEG 4000. CRUMLIN-PEDERSEN, Ole; OLSEN, Olaf; BONDESEN, Erling - The Skuldelev ships I…

[338] HÅFORS, Birgitta - The Role of the *Wasa*... p. 195-216.

[339] HOFMANN, Per b) - On the Stabilization of Waterlogged Oak with PEG...

treatment solution should be composed almost completely of PEG 3350 with very little PEG 200, whilst for sound wood it suggests the reverse[340]. This mixture of different PEG molecular sizes will allow a better impregnation and bulking; and also enable a quicker stabilization of slightly or heavily degraded materials[341]. Since PEG with lower molecular weight does not present a great difference from water, starting the impregnation with it and with a low concentration (10%) and gradually increasing the concentration (steps of 10-20% until 95% is achieved) will allow water to move slowly from waterlogged materials, preventing osmotic collapse[342]. As for PEG 3350, it should be added in steps of 5-10%.

The PEG solution and increment will depend on: i) the size of the objects, if artifacts are small, bigger increments can be done, on the other hand, for larger artifacts, smaller increments; ii) the extent of deterioration, the more deteriorated, the higher concentrations can be used in each increment; iii) the speed of treatment needed, shorter treatment times require a higher concentration in each increment. Also, in the case of wood, the density of it is important, less dense (<0.4 g/cm^3) species can have higher concentrations of PEG in each increment while denser (>0.6 g/cm^3) species require lower concentrations.

Due to the fact that this is a long process during which microbial growth can arise, causing decay into materials and enabling PEG penetration, to avoid this microbial growth a biocide can be added to PEG solutions[343].

The PEG itself does not remove water as it is just considered a pre-treatment that confers mechanical strength to materials, preventing high shrinkage and distortion rates. This means that materials still need to be dried without affecting their structure. The drying can be achieved through different techniques, the most common being air drying and freeze-drying.

Air drying is a process in which water is removed by evaporation and it is particularly used for big objects, such as hull timbers. However, despite being a simple and inexpensive technique it can result in high shrinkages rates, stress and excess of dehydration and collapse of the structures. To avoid these situations moisture removal must be controlled, which is achieved by controlling the humidity environment.

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[340] COOK, C.; GRATTAN, D. W. a) - A Method of Calculating the Concentration of PEG.

[341] GRATTAN, D.W.; COOK, C. b) - A Practical Comparative Study of Treatments for Waterlogged Wood...

[342] GRATTAN, D. W. a) – *Op. cit.*

[343] BJÖRDAL, C. G; NILSSON, T. - Observations on Microbial Growth during Conservation…

Artifacts are introduced in a high humidity environment which is lowered in stages, until equilibrium and humidity grade required for storage or display is reached[344].

In the freeze-drying process, surface tension, capillary forces and shrinkage are solved by sublimation (also called lyophilization) of water from the artifacts. In this situation PEG will act as a structure protector, avoiding the volume increase by the crystallization of water during freezing.

Freeze-drying is done by placing the artifacts in a freeze-drying machine or chamber, where the objects can totally fit into it, where they are very rapidly frozen [345]. The temperature is very low (–28 and −40ºC) freezing and separating all elements until the eutectic concentration is reached. During this stage and because PEG is quite mobile, its viscosity very low and drying very slow, it penetrates the cell walls and replaces the sublimate water making the solution enriched with this element.

To monitor the freeze-drying two processes can be performed, the removal of artifacts from the freeze-drier and weighing the artifacts, until the ideal weight loss is achieved, or, in the case of woods, use the computer program PEGcon. This program was developed by the Canadian Conservation Institute (CCI)[346] and besides helping in the freeze-drying process, it helps to better adjust PEG concentrations according to the condition of materials, weights and volumes. The only requirement for the use of this program is to know the wood species and the actual density, the maximum moisture content at fiber saturation point and the normal density[347].

If the treatment was well carried out the materials should present no loss of details. Also it can be submitted to restoration and handling. If the artifacts present excess of PEG it can be removed with hot air, infra red lamps, through ethanol swabs[348] or with hot water[349].

Although it can be a good choice for cellulosic, keratin or collagen materials[350] the use of PEG is restricted and cannot be applied to all materials. PEG must not be employed in composite object, such as hulls with iron nails or tools with organic and

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[344] HÅFORS, Birgitta – *Op. cit.* p. 204-205.

[345] There are several publications describing theoretical principles of conservation with freeze-drying method, and articles that present installations and parameters that must be developed for the process see among others: JENSEN, P.; SCHNELL, U. - The implications of using low molecular weight PEG…; GRATTAN, D. W.; CLARKE, R. – *Op. cit.* ; WATSON, Jacqui - The freeze-drying...

[346] COOK, C.; GRATTAN, D. W. a) – *Op. cit.*

[347] *Idem*, p. 239-252.

[348] MURRAY, Howard - The Conservation of Artifacts from the Mary Rose...

[349] HAMILTON, Donny L. a) – *Op. cit.* p. 27-28.

[350] CAMERON, E; SPRIGGS, J.; WILLS, B – *Op. cit.* p. 248-250.

metal materials, since it is a slightly acidic solution, which makes it able to corrode metal[351]. Also it cannot be used in painted or lacquer waterlogged wooden objects, since it promotes the detachment of the layers[352].

Despite being the chemical most commonly used for impregnation or bulking, PEG does present some problems and has some limitations. One of these conservation concerns is hygroscopicity, which makes it very unstable at a relative humidity above 65%. This can lead to two different problems, one related with the draw out of PEG, leaving open cavities which will lead to the collapse of the internal structure; and the other associated with the transport of salt solutions from inside of the wood to the surface, where precipitation takes place, leading to degradation[353].

Another situation is the oxidation of PEG, a consequence of the high temperatures to which it must be subjected during the impregnation. At room temperature PEG is a semi-liquid or gel (for a molecular weight of between 1000 and 1500) or it presents a waxy appearance (molecular weights higher than 3250)[354]. Due to this fact, to achieve a better solubility in water and to reduce the impregnation time, for several years, PEG grades of molecular weight over 600 were heated during treatments. However, besides high temperatures darkening the surface and decreasing the pH and molecular weight of PEG[355], it is now proven that heat promotes chain scission, thus its degradation[356].

Other concerns about the PEG treatments are the weight increase of artifacts, and its considerably unnatural dark appearance.

Also, it is not a simple treatment to perform. Calculating the concentration and amount of PEG that is required to bulk and to impregnate each material along with its distribution and penetration is a difficult task. PEGcon is really helpful, but only for wood treatments and still requires some accurate information about the wood species.

Finally, the long amount of time required to carry it out, the high cost and facilities needed, especially if freeze-dry equipment is necessary, make this treatment quite limited.

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[351] MACLEOD, I.D.; RICHARDS, V.L.; FRASER, F.M. - The PEG water solvent system…
[352] HÅFORS, Birgitta – *Op. cit.* p. 215-216.
[353] SANDSTRÖM, Magnus; [*et al.*] a) - Acidity and Salt Precipitation on the *Vasa*...
[354] HAMILTON, Donny L. a) - p. 27-28.
[355] BILZ, M; [*et al.*] – A Study of the Thermal Breakdown of Polyethylene Glycol...
[356] PADFIELD, Tim; [*et al.*] - Decomposition of polyethylene glycol (PEG) on heating...

In Portugal, PEG treatment has been developed since 2003, this was the chosen method to stabilize the *Ria de Aveiro A* hull[357]. The treatment is being carried out in two steps, which corresponds to the application of PEG with two different molecular weights, 400 and 4000, in tanks designed for this purpose, equipped with a recirculation system, heating and filtering[358]. Initially PEG 400 was applied to a maximum concentration of 20%, followed by PEG 4000. In the last step, PEG has been applied with increments of 2% a month, until 70% is achieved. After the impregnation, control drying will be performed in a climatic chamber, also built for this purpose. To inhibit the growth of microorganisms a biocide was added to this PEG solution.

19.3.2. Silicone oils and conservation

Silicones, also called polymerized siloxanes or polysiloxanes $[R_2SiO]_n$, are considered a semi-organic compound, with inorganic backbone (Si-O) and organic side groups, with these last ones attached by silicon and carbon bonds (Si-C).

Since its synthesis in 1824, by Jön Jacon Berzelius, siloxanes have been used for multiple applications. Their first documented use in conservation was in 1923, for stone consolidation; since then they have found innumerous applications in conservation practices, as a consolidant of stones, brick or wood with significant success for preservation. Their ability to be employed in many materials lies in the fact that siloxanes can be synthesized in a wide of viscosity (liquid/oil, gums, gels, elastomer and resin), properties and compositions; all chemically stable, even when heated, biologically inert (no microbial growth) and resistant to oxidizing agents (including UV) and also to acids and bases.

The most used siloxanes in the consolidation of stone and in the conservation of waterlogged archaeological materials are especially the alkoxysilanes, best known by the generic term of silicone oils.

Treatment of archeological remains with silicone began with *plastination*[359] followed by other experiments[360]. Only with the investigations, carried out by

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[357] ALVES, F. [*et. al.*] a) – *Op. cit.*

[358] COELHO, João; GONÇALVES, Pedro; ALVES, Francisco - Conservação das estruturas em madeira de um navio...

[359] VON HAGENS, Gunther; TIEDEMANN, Klaus; KRIZ, Wilhelm - The current potential of plastination...

professors Dr. Donny L. Hamilton and Dr. Wayne C. Smith, at Texas A&M University (TAMU) and Dr. Jerome M. Klosowki from the Dow Corning^{TM} Corporation, preservation through silicone oil achieved successful results.

Aiming for the recovery of waterlogged archeological artifacts from *La Belle* shipwreck[361] they first started with experimental studies with dimethyl siloxane hydroxyl terminated polymers, different combinations of cross-linkers, and catalysts[362].

The basis of the process was to study the nature of artifacts, their porosity, size and their preservation degree. These allowed a better understanding of the materials needed and a better choice of silicone oil, which could provide a good consolidation of the structure. The chosen silicone oils, presented a low and medium molecular weight, which means low and medium viscosities[363], thus a better ability to impregnate materials. In other situations a mix of silicone with different viscosities were used[364]. By blending two different viscosities fluids it was possible to achieve a viscosity that met the artifacts needs of consolidation. In both situations about 3% to 20% (v/v) of methyltrimethoxysilane (MTMS) $[(CH_3O)_3\ SiCH_3]$, a cross-linker, was added.

The cross-linker is also a silicone molecule, but it presents multiple functional sites that react and link with the silicone polymer to form a more complex, viscous and stable polymer which, in most cases, implies a better cell penetration and also a longer shelf life.

After impregnation, a catalyst is introduced either by coating the artifacts surface or just by subjecting the objects to its vapor, for a period from 24 to 48 hours[365]. In those experiments dibutyltin diacetate (DBTDA) $[C_{12}H_{24}O_4]$, was considered to be best catalyst for preserving organic artifacts[366]. As a catalyst has the ability to increase the rate of chemical reactions, in this case it penetrates deep into the material structure and, in reaction with moisture, enables the polymerization of siloxanes, coating the cell.

Finally, the artifact is put out in fresh air allowing its cure and the catalyst vapor to completely dissipate.

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[360] DE LA CRUZ BALTAZAR, Vera – Plastination as Consolidation Technique...

[361] BRUSETH, J; TURNER, T. – *Op. cit.*

[362] SMITH, C. Wayne a) – Archaeological Conservation Using Polymers…

[363] The molecular weight of a silicone is directly related to the degree of polymerization (DP), the greater the polymerization degree, the higher is the molecular weight, the higher the molecular weight, the higher viscosity will be and more slowly will be the flow into a material. Silicone can present a viscosity from 0.65 cTs, which is thinner than water, to more than 20,000,000 cTs, thicker than rubber.

[364] SMITH, C. Wayne a) – *Op. cit.*p. 24; 70; 84.

[365] *Idem*.

[366] *Ibidem*, p. 11.

The use of these alkoxysilanes was part of a treatment technique developed at the same time. This strategy begins with solvent dehydration baths, in which all water is progressively taken out of the interior of materials. Since silicone oils do not mix with water, all free-water must be removed to allow silicone impregnation[367]. These baths begin with 25% (v/v) ethanol and 75% (v/v) deionized water (DI), followed by the progressive introduction into new solvent baths with 25% increments each, until 100% ethanol is reached. The second step of dehydration process is to introduce acetone into the materials structure following the same procedure as ethanol. These baths occur in a progressive way to avoid stress and possible structure ruptures, forced by the osmotic pressure. The time of staying in each baths will depend on the size, nature and preservation degree of the artifacts, but should not extend more than 4 weeks per bath. Vacuum can also be used[368].

The next step is impregnation, which begins with the transfer from the last bath of acetone (100%) to a container with the chosen silicone oil and, according to the material to preserve, a percentage of MTMS. The transfer stage has to be fast, so that no evaporation of the solvent occurs. After being in the container, and because materials tend to float, a mesh and weights are placed upon the objects. The impregnation itself starts by placing the container in a vacuum chamber, where a sequence of pressures is applied; starting with a vacuum of 40.64 kPa until a vacuum pressure of 67.73 to74.5 kPa is progressively achieved[369]. The final stage of impregnation is to slowly reduce the vacuum until ambient pressure is attained. The time in each pressure stage should be maintained from 30 minutes to 48 hours, and the last one kept for 24 hours.

After the removal of artifacts from the silicone bath/treatment, they must be placed on a net to drain, for 48 hours at least, the polymer mixture excess. This is followed by mechanical and chemical cleaning of the surface with swabs, soft brushes and paper towels embedded with MTMS, which will work as a solvent. Draining the excess of silicone allows not spending so much MTMS during the cleaning and also the drained materials can be stored and reused in another treatment.

The last step of the silicone oils treatment is the polymer cure by deposition of a catalyst, which can be applied by vapor deposition or by topical application to which the artifacts are subjected for a minimum of 24 hours. In the first technique, objects are

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[367] *Ibidem.*

[368] Smith, C. Wayne; Hamilton, D. L.; Klosowski, J. - Silicone Oil…

[369] *Idem.*

placed in a container or plastic bag with a tin containing a small amount of this product. In the second one, the surface of the remains is brushed with the catalyst and then sealed and placed in a plastic bag or container.

In the past the Archaeological Preservation Research Laboratory (APRL) and the Conservation Research Laboratory (CRL), at TAMU, have been using these techniques in almost every waterlogged piece, being recognized worldwide for their good results. No doubt that despite the number of steps and the several silicone oils and cross-linker combinations to choose from, it is an easy procedure to implement, which allows the recovery of organic and inorganic materials, and also composite objects.

Many times composite materials require divergent approaches, often forcing the disassembling of artifacts, sometimes with losses. Through silicone oil treatments it is possible to conserve all with no material loss. On the other hand, if an object is so fragile that it requires consolidation prior to cleaning, it is possible to do this with alkoxysilanes, since they can impregnate materials without permanently clinging to each other.

Thanks to cross-linked silicone oils, organic materials get a protective film at the surface. Also due to the ability of these compounds to establish covalent chemical bonds, the structure is reinforced, gaining strength and flexibility, without filling the cellular structures of the wood[370] or without transforming the proteins, thus, without creating stress or big dimensional changes, even when it is cured.

There are other advantages of using cross-linked siloxanes to preserve waterlogged archaeological organic remains. The treatment is not expensive, the equipment needed can be typically found in any conservation laboratory, thus it is not necessary to make an acquisition to that end, and the efficiency of polymers, even with the continuous reuse of the drained polymers, shows that economically it is a good option. Another advantage is that the time required for a complete treatment is substantially lower, especially when compared with PEG. Also to be able to choose from a molecular weight, organic functionality and a polymer structure represents unlimited possibilities and results. Finally, it presents such longevity[371] and is so stable that it withstands long time storage[372], or exhibition, in adverse conditions, since it is

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[370] CABRERA TEJEDOR, C. - Re-Conservation of Wood... p. 178.

[371] Since the last 25 years number of studies has been conducted which show that the silicone has a minimum life expectancy of 200 years. SMITH, C. Wayne b) - Silicone and Polymer Technologies...

[372] HAMILTON, Donny L. a) – *Op. cit.*

not sensitive to fluctuations of humidity and does not oxidize in the presence of UV or other oxidizing agents[373].

Despite of all these advantages silicone must not be seen in a naive way. Bulking materials and cross-linkers can change according to each artifact, thus it is not possible to say which molecular weight is better to each organic material without a precise analysis. In addition, the use of polar organic solvents such as ethanol, acetones or others during solvent dehydration must be considered with great care, since such chemicals may dissolve oils and tannins, destroying aesthetic effects and structure[374]. Also, regardless of the type of material a slight change in the surface color is possible to happen, objects acquire a brighter tone, which is not always clearer, causing a surface finishing misinterpretation. Furthermore, since silicone oils act at a molecular level, when cross-linked the polymeric chain does not present defined solubility parameters, thus this treatment is still considered non reversible.

19.3.3. Acetone/Rosin method

After verifying the limitations of PEG, especially for the conservation of well preserved waterlogged hardwoods, H. McKerrell, E. Roger and A. Varsanyi developed, in 1972, a new bulking procedure, implying acetone and rosin, the acetone/rosin method[375].

The aim of this process is to consolidate wood by filling the spaces with rosin. Rosin, also called colophony or colophony resin, is a solid, friable and semi-transparent resin, soluble in most solvents[376]. After melting, it quickly hardens forming a bond that will strengthen the materials and reduce the stress of drying.

The procedure starts by a pretreatment with 3 to 5% (w/w) of hydrochloric acid (HCl), followed by a dehydration with acetone (depending on the thickness of the wood, three or four successive baths over a period of two weeks each) until a moisture content less than 1% is achieved. This phase is very important, since water is incompatible with rosin, it is imperative to remove all free water before the consolidation begins.

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[373] GODFREY, I.; [*et al.*] – *Op. cit.*

[374] KITE, Marion; THOMSON, Roy; ANGUS, Aline – *Op. cit.* p. 125.

[375] MCKERRELL, H; ROGER, E.; VARSANYI, A. - The Acetone/Rosin Method...

[376] HORIE, C. V. – *Op. cit.* p. 248.

The artifacts are placed inside a container and impregnated with a solution of 67% (w/w) rosin and acetone. According to researchers, to be able to penetrate inside a wood structure it is necessary to melt it, so it must be heated to 52ºC[377]. Depending on the thickness of the objects, the time treatment may last from two weeks to several months. For example, artifacts less than 5 cm thickness require two weeks treatment, while others with 5 to 10 cm thick can be treated in 4 weeks[378].

The impregnation can also be performed at room temperature and make use of other solvents, such as ethanol and isopropanol, but then treatment time increases significantly, from six to twelve months[379].

After the consolidation stage, objects are removed from the containers and then air dried. If there is an excess of rosin at the surface, it can be removed through swabs or brushes with acetone or by wrapping the artifacts in bandages with this solvent.

Acetone/rosin is a very effective procedure which has been implemented worldwide. At a physical level it is light in weight, there is no crack formation or dimensional changes, and if they do exist they are minimal. Besides, it presents very good results at an aesthetic level, since the shape of the artifacts and surface details are maintained and also the color and texture correspond to a non degraded wood[380]. In addition, within a certain period, it is considered a reversible treatment, since rosin can be extracted without loss of wood materials[381]. Because it is not susceptible to humidity changes, it is a good choice for storage or display when preventive conservation measures cannot be assured.

This method can also be used in composite materials, such as wood with metal, but it must be done without the hydrochloric acid pretreatment.

When compared with other treatments, it is not the most expensive and with the exception of a fume hood does not require major laboratory equipment.

Without a doubt the major disadvantage of this process is the flammability of the acetone, with special concern during the heating process. This is also the reason why this method is not recommended for large waterlogged wooden finds, since large objects imply a greater amount of solvent.

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[377] MCKERRELL, H; ROGER, E.; VARSANYI, A. – *Op. cit.* p. 120.

[378] *Idem.*

[379] HAMILTON, Donny L. b) – Conservation of Cultural Materials… p. 311.

[380] Several authors have referred that acetone-rosin treatment increase strength in objects along with a light color. HOWARD, Brian R. - Acetone-rosin Treatment...

[381] GRATTAN, D. W.; CLARKE, R. – *Op. cit.* p. 187.

There are other disadvantages, such as it cannot be used in wood that appears to be in poor condition. Also, the colophony tends to oxidize making the wood fragile, so despite being less susceptible to changes in the relative humidity, it does not mean that it can withstand long time storage or display. Finally, due to the fact that rosin is very brittle and it does not bend, if it becomes necessary to flex a piece of wood, rosin would not allow such movement and the wood, eventually, would break[382].

19.3.4. Sucrose stabilization method

The earliest known approach using sugar for wood stabilization was reported in 1904[383], in 1965 sucrose is mentioned as a possible conservation material for the Bremen Cog[384], but it was only in the 1970s that the treatment of waterlogged wood with sugar solutions was referred to, continuing its use until the present days[385].

Sucrose is a disaccharide composed of glucose and fructose ($C_{12}H_{22}O_{11}$) with a molecular weight smaller than PEG, commonly known as table sugar or saccharose, it is a white, odorless and crystalline powder, non-toxic, non-flammable, non-hygroscopic, readily soluble in water, difficult to dissolve in ethanol and insoluble in diethyl ether or acetone.

The preservation method using pure sucrose starts by impregnating the wood artifacts with a 5% (w/v) solution of sugar, dissolved in water at room temperature[386]. After soaking the materials, temperature gradually increased to 50°C, and maintained until the bulking is complete. Besides allowing a greater and more consistent penetration of sugar, heating the solution will also help to control fermentation[387].

After two-week intervals the sucrose solution receives an increment of 5% (for woods with light specific weight[388]) or 10%, until 45% is reached. The wooden objects are kept in this solution until it achieves equilibrium, which is determined by the cessation of weight gain by the wood. For a better understanding of the bulking agent penetration rate every time that a solution is changed, the artifacts, or a chosen

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[382] HAMILTON, Donny L. c) – Conservation of Cultural Materials from Underwater Sites. p. 311.

[383] In 1904 W. Powell applied for a patent for the stabilization of wood with sugar solutions in both the United States and Germany. STAMM, A. J. - Minimizing wood shrinkage and swelling…

[384] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke – *Op. cit.* p. 423.

[385] *Idem*, p. 423-426.

[386] PARRENT, James M. b) - The Conservation of Waterlogged Wood Using Sucrose… p. 63-64.

[387] RODGERS, Bradley A. - *Op. cit.* p. 50.

[388] *Idem*.

representative artifact, are weighed. As in other procedures the reason for these gradual increments is to minimize the osmotic pressure.

The last stage is the gradual increase of the solution, by 10% increments, until a 100% (w/v) solution is obtained[389]. After two weeks in that solution the artifacts are removed and placed in a controlled environment, where they are slowly allowed to air-dry[390].

Following the drying all surfaces are easily cleaned with swabs, brushes or cloths impregnated with a small amount of water.

The sucrose method presents great advantages at an aesthetic and physical order as the wood presents a natural color and a medium weight, and depending on the wood species and its deterioration level, it brings high dimension stability with less shrinkage when compared to PEG treated wood[391]. Another benefit is that it is reversible and also allows the use of glue, however, when joining it is necessary to point out that sucrose does not allow the bending of the material. Since sucrose is not corrosive it has no risks for the operator or to the environment, so it does not need special safety equipment, storage or disposal. In addition, it has a low cost budget, the sugar is inexpensive, easy to find and the treatment itself is simple to perform, not requiring great laboratory facilities and in fact it can be started on-site.

The development of this method on wood composites materials is contradictory, since it is not a corrosive substance, so it should be applied without metal corrosion occurring, but it is not recommended because it is suggested that the metal can corrode while submerged in a heated sugar/water solution[392]. Thus, a small composite artifact can be saved through this process, whereas for a bigger one this treatment is not an option.

For wood with low levels of deterioration this method seems to present very good results, especially considering Anti-Shrink-Efficiency (ASE)[393]. However, more degraded wood appears to have great changes, its stabilization being very unpredictable[394].

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[389] PARRENT, J. M. a) - The conservation of waterlogged wood using sucrose… p. 39-40.

[390] “Submitting the wood too quickly to conditions of low humidity will damage it. Slow, controlled drying and adjustment to the prevailing atmospheric conditions”, HAMILTON, Donny L. a) – *Op. cit* p. 29.

[391] HAMILTON, Donny L. c) – *Op. cit.* p. 309.

[392] *Idem.*

[393] HOFFMANN, Per a) - Sucrose for stabilizing waterlogged wood…

[394] HOFFMANN, P. – Sucrose for the Stabilization of Waterlogged Wood II…

As for the speed of the treatment, sucrose readily penetrates wood, so impregnation can be relatively quick for small artifacts; however, for thick woods it is a long time process, almost identical to PEG[395].

As for drawbacks there are a few that must be considered. During impregnation at percentages less than 40% fermentation is possible to occur, in order to prevent microbes and insects from reaching the solution, resulting in a biological breakdown of the sucrose and in the production of acetic acid, biocides must be added to the solution[396]. If tanks are kept uncovered it is possible to for the loss of concentration and also biological breakdown to occur[397]. Thus for these reasons treatment must be constantly supervised, being aware of foam appearance, odors and its concentration.

Until now the ability to resist long-term storage or display has been little known. Nevertheless it has already recognized been the need to maintain artifacts treated with sucrose in a controlled atmosphere since it has the ability to retain moisture and as a result materials should be stored under conditions of less than 70% humidity.

For other preventive conservation assumptions, such as biological decay, especially from insects, there have been inconsistent reports: some investigations suggest a severe attack from termites and soft rot and brown rot fungi, while others just suggest a biological susceptibility to it[398].

In order to decrease the risks of deterioration it is necessary to have physical monitoring of collections, although it does not mean that special care is required. In fact these recommendations are quite similar to the environment needs required in other treatments.

There are other sugar-related treatments, such as sugar alcohols sorbitol[399], mannitol[400] lactitol, and maltitol, which have shown interesting results, especially sorbitol when added to cane sugar and the lactitol[401]. Despite the positive outcome in particular with dimension stability, heat stability, low hygroscopicity and microbiological stability, they still present some issues which must be solved before advising this treatment. On the other hand, when compared with sugar treatment they

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[395] HOFFMANN, Per a) – *Op. cit.*

[396] MORGOS, Andras; STRIGAZZI, Giancarlo; PREUSS, Helmut - Microbicides in sugar conservation...

[397] Due to the lack of monitoring the Poole Logboat suffer from biological breakdown of the sucrose and loss of concentration. Cf. HUTCHINGS, Jeremy; SPRIGGS, Jim - The Poole logboat...

[398] UNGER, Achim; SCHNIEWIND, Arno P.; UNGER, Wibke – *Op. cit.* p. 426-428.

[399] COOK, C; GRATTAN, D. W. b) - A practical comparative study of treatments for waterlogged wood, part III: pretreatment solutions for freeze-drying.

[400] MURRAY, Howard b) - The use of Mannitol in freeze drying...

[401] IMAZU, Setsuo; MORGOS, Andras – Conservation of Waterlogged Wood Using Sugar Alcohol...

require more experienced hands and they are still more expensive than other treatments and so for this reason such methodologies are not presented in this thesis.

19.3.5. Supercritical drying

In 1822, Charles Cagniard de la Tour noted that at a certain temperature the densities of a liquid and gas phases became equal, i.e., a supercritical fluid (SCF) phase. A few years later, Thomas Andrews reported that SCF can dissolve some solids and liquids. In 1879, Hannay and Hogarth reported that increasing the pressure a precipitate from a SCF can change its physical form, effusing through solids like a gas, and dissolving materials like a liquid[402]. Experiments with SCF continued until the 1970s, a time when they were considered a good alternative to liquid extraction and distillation.

A liquid matter, depending on its nature, is more or less dense and the particles are not attached, sliding over one another (e.g., they adapted themselves to the shapes of the containers thereof). However, there are still mooring forces between them, so their volume does not vary. At the gaseous state, substances present lower density than solids and liquids occupying the entire volume of a container where they are placed. They can expand indefinitely and are compressed with great ease. This behavior can be explained by the forces of attraction between the particles which are very weak, therefore, presenting high mobility.

In supercritical drying (SCD) a liquid is removed by a controlled way, which is possible due to the diffusivity of SCF and its low viscosity, which gives it the ability to penetrate solid materials, and the power of dissolution of the liquids forms. Basically the principle of SCD happens when the material is placed in contact with an SCF, and the volatile substances are dissolved into the supercritical phase. After this dissolution the SCF, which holds the dissolved substances, is removed from the material. In most processes the extracted component is separated from the SCF, by means of a temperature or pressure, allowing the recycling of the SCF and its new use.

This process is possible since in a SCF, the three phases (liquid, solid and gaseous) converge at a single point at a given temperature and pressure, called the triple point, coexisting in a thermodynamic equilibrium. Above this point, at the critical point,

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[402] HANNAY, J. B.; HOGART, J. – On the solubility of Solid in Gases…

or critical state, which happens either by increasing pressure (critical pressure) or by increasing temperature (critical temperature), or composition, the phases become inseparable. Thus, by manipulating pressure and temperature, a fluid can dissolve different elements, with different solubility[403]. On the other hand, besides manipulating temperature or pressure to achieve a higher solubility, it is possible to increase solubility by increasing the density. Along with these parameters, other proprieties such as viscosity, thermal conductivity, diffusibility and surface tension, allow SCF to have outstanding removal capabilities that will also enable the extraction of the desired compounds.

The process of SCD is very difficult to manage since temperature and pressure must be controlled, thus special equipment is required. Also a SCF is needed, carbon dioxide (CO_2) being the most used. Despite its limited ability to dissolve polar molecules, it presents low critical parameters (31.1°C, 73.8 bar), non-toxicity, inflammability, good solving properties, inertia and the ability to be easily separated from the materials.

Obviously, the use of SCD in waterlogged archaeological organic material conservation is related with its ability to remove water without causing surface tension or other distortions caused by drying effects and it could be applied to different organic materials, such as wood, cork, rope or bone, and composite materials.

Nevertheless, to be able to completely eliminate the water, 347ºC and 220.5 bar is needed, which means that the required temperature would degrade organic materials[404]. On the other hand, if materials contained a bulking element such as PEG, this would also lead to degradation of this polymer, once it can be degraded above 70ºC[405]. Considering this situation it is then necessary to use an SCF with a lower critical temperature and pressure. Because carbon dioxide is not sufficiently miscible with water, it is necessary to use a fluid miscible with both, such as methanol (CH_3OH), ethanol (CH_3CH_2OH), ethyl acetate ($CH_3COOCH_2CH_3$) or acetone ($CH_3(CO)CH_3$).

So, within the SCD for waterlogged archeological organic materials the treatment must have three steps: the first usually involves replacing water with methanol[406], which has small molecules so no problems with osmotic pressure occur.

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[403] REGER, D.; GOODE, S.; MERCER, E. – Química … p. 470.

[404] PADFIELD, Tim – *Op. cit.*

[405] PADFIELD, Tim; [*et al.*] – *Op. cit.*

[406] Cf. KAYE, Barry; COLE-HAMILTON, J.; MORPHET, Kathryn – Supercritical Drying … p. 236-238.

The artifacts are impregnated with methanol until the water content is less than 1%. In the second step artifacts are placed in a chamber, above 50ºC and 95 bar, where they are exposed to supercritical carbon dioxide. With this exposure, both fluids connect and methanol is then extracted through carbon dioxide. During this stage carbon dioxide replete with methanol is conducted to a chamber where the temperature and pressure are reduced until 40ºC and 35 bar, allowing the recycling and reuse of carbon dioxide. The last step is a slow decompression of the supercritical carbon dioxide from the artifacts, without creating tension.

The reason for the use of methanol is based on its capabilities to mix with carbon dioxide, its inexpensive cost and its biocide characteristics, avoiding the need for using a biocide. The only drawback is the hazard character of methanol, being highly flammable and toxic.

The SCD treatment is a faster process, when compared with PEG or freeze-drying. Also, no chemicals are left in the artifacts, and it is completely reversible, since it is possible to rehydrate the artifacts under a vacuum condition. Other advantages are mainly physical as objects conserve the original surface, color, brightness, and weight, with high mechanical resistance. Over the course of time artifacts appear to be stable, withstanding storage and display conditions with no need for particular care rather than the normal preventive conditions required for each organic material.

Despite all these advantages this method cannot be performed in all types of materials, especially in more degraded ones. Usually in these cases, there are differences between the less degraded interior and more degraded surface, so during the drying process the tension created, by this differential, causes components to break which corresponds to shrinkage and consequent cracking of materials, which is particularly serious in degraded woods[407]. However, if the wood is impregnated with PEG the retraction is substantially reduced, since highly degraded areas are first stabilized[408].

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[407] SCHINDELHOLZ, Eric - An Evaluation of Supercritical Drying and PEG/Freeze…

[408] TESHIROGI, Miho; [*et al.*] - Conservation treatment of waterlogged wood...

19.4. Preventive conservation

The preservation of waterlogged archeological organic material involves its stabilization not only by conservative interventions, but also by taking measures that include the care and management in storage or display, i.e., preventive conservation measures.

The interpretation of preventive conservation has been widely presented since its introduction by ICCROM in 1975[409]. Basically its main purpose is to reduce deterioration, by carefully evaluating materials, their chemical and physical features, relating them to potential risks. These risks are divided into chemical mechanisms, associated with environment and its microclimates, and physical forces, related with handling, theft and vandalism.

19.4.1. Environmental factors and their effects

The environmental factor is considered to be the most silent enemy, whose harmful effects require prevention. Nevertheless being a common statement, there is no doubt about the impact of temperature, humidity, light and pollutants upon artifacts.

Temperature is related with the thermal energy transfer to materials, which is able to produce direct or indirect internal tensions on objects, since they change their physical characteristics as they absorb or released heat[410]. When temperature rises, the amount of absorbed energy increases, causing major molecule vibration, which is responsible for the increase of the internal stress. In turn, this will result in a lack of strength in materials. On the contrary, if the temperature drops, materials turn stiff and brittle. Thus, temperature influences hydrolysis rates and degradation.

Another factor affected by temperature is the Relative Humidity (RH). The RH is defined as the ratio of the partial pressure of water vapor (H_2O) in a mixture of saturated vapor pressure of water at a given temperature on a particular system; it is dependent on the pressure and temperature in it. Thus, when temperature rises, RH decreases, causing materials to dry, shrink or become more brittle. On the other hand, if temperature falls, RH is forced to increase and organic materials, which are mostly

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[409] PUTT, N.; MENEGAZZI, C. - ICCROM preventive conservation experiences...

[410] CAMUFFO, Dario – The role of temperature and moisture… p. 11.

hydrophilic, will absorb moisture and swell. There may also be differences within the material during a rapid fluctuation or successive fluctuations of RH which cause local expansions, causing internal tensions that can turn into fractures[411]. From a chemical point of view, water molecules can change, being more inert simply by connecting at the material's surface, in the first case of low RH; or just more interactive with materials, bonding with elements such as hydrogen, every time that RH gets higher[412].

Light is another fundamental deterioration factor, but it is also essential to communicate the information held in an artifact, providing a context in time and space for the researcher or for the museum visitor[413]. Basically, light is a electromagnetic radiation that present a wavelength (λ) in a range about 380 nanometers (nm) to about 740 nm, with a frequency (v) range of about 405 THz to 790 THz. In other words light is energy. It can be characterized by its properties such as intensity, propagation direction, frequency, wavelength spectrum and polarization. When the electromagnetic radiation strikes an artifact some amount of energy (photons) penetrates it and different photochemical degradation occurs. This phenomenon depends on the kind of energy and the type of molecules in the object affected[414]. According to the energy type and amount, so it has the ability to rearrange and break molecular bonds, weakening the materials. Higher frequency (short wavelength), like UV radiation, causes more and faster photochemical degradation, as this radiation normally exceeds the required activation energy for the majority of molecules. On the other hand, if the frequency is lower (long wavelengths), such as IR radiation, its energy is reduced and so is its ability to induce an excited state in the molecules.

The primary photochemical reaction is photo-oxidation, which in a macroscopic level is expressed in terms of photosensitivity or light-fastness. This is followed by photo-reduction, in which occurs the addition of electrons into an already photo-excited molecule, causing its alteration. Finally, photo-fragmentation occurs, which results in the rearrangement or fragmentation of a molecule after a bond cleavage[415]. All of these have visible effects, such as chromatic variation with changes in colors, either by fading or yellowing, or a mechanical effect, like fibers destruction or brittleness[416]. Considering the photochemical effects and their cumulative and irreversible character

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[411] MICHALSKI, S. b) - Guidelines for humidity and temperature...
[412] CAMUFFO, Dario – *Op. cit.,* p. 17-28.
[413] SHAW, Kevan – Museum Lightning...
[414] BACCI, M.; CUCCI, C. – The role of light…p. 59-68.
[415] *Idem*, p. 63-64.
[416] MICHALSKI, S. a) - Damage to Museum Objects...

[417], new approaches have arisen. However, despite all the studies the guidelines to the light effects mitigation, generally, are almost the same since the beginning[418]. The basic strategy is to: i) lower the illumination levels, but taking into account the visual needs of the public; ii) use the classification of materials according to their sensitivity to visible light (Table 3); iii) reduce the light exposure time to the necessary; iv) eliminate non visible radiation, such as UV and IR.

Besides these degradation aspects, radiation also has the ability to trigger thermal differences in objects, when a beam of light strikes the surface the temperature rises leading to internal stress.

Table 3 - Sensitivity of organic matter to visible light.

Category of light sensitivity	Description
1. Irresponsive	The object is entirely composed of materials insensitive to light: enamel.
2. Low responsivity	Durable materials that are slightly responsive to light: undyed leather, wood, horn, bone, ivory.
3. Medium responsivity	Materials that are moderately responsive to light: textiles, botanical species, fur and feathers
4. High responsivity	The materials are highly light-responsive: silk.

(Adapted from BACCI, M; CUCCI, C. – The role of light, p. 66.)

Another risk associated with temperature RH and light is the possibility of microclimates formation. Many rooms or artifacts present different temperature gradients, either due to heaters or lamps, or even due to airflow, thus conducting to a direct action on RH gradients which will lead to pockets of humidity or condensation formation.

As for pollution, the action of certain compounds can induce chemical reactions to an object's surface causing its degradation[419], most of the time only recognized by its effects on the object's surface. Pollutants are grouped into gases, aerosols, liquids or solid particles, divided according to their nature in three different ways: airborne, with an anthropogenic or natural origin carried by the air, also pollutants transferred by materials used in storage or display and pollutants that already exist as a part of the

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[417] THOMSON, Garry – *Op. cit.*, p. 2-65.

[418] MICHALSKI, S. c) – Towards specific lighting guidelines....

[419] The standards for pollution in museums and the results of the chemical reactions of those upon artifacts are provided by TÉTREAULT, Jean a) – Airborne Pollutants in Museums, Galleries and Archives...

artifacts (Table 4). The most known airborne pollutants include carbon particles, carbon monoxide and carbon dioxide, nitrogen, sulfur dioxide, acid acetic and ozone. The extent of deterioration upon organic objects includes chemical and structural damage caused by oxidation, moisture on the artifacts surface and surface staining[420].

Another threat is microbiological growth. Biological decay is directly related to temperature and RH, with fungi and insects more often responsible for the damage. However, controlling RH below 65%, then biodeterioration is prevented.

Table 4 - Pollutants effects on objects.

Pollutants	**Nature**	**Effects**
Airborne pollutants	Atmospheric sources: ozone, hydrogen sulfide, carbonyl sulfide, sulfur dioxide, nitrogen dioxide, and particles. From emissive products, objects and people: Sulfur-based gases, organic acids and particles.	Acidification of cellulosic fibers, discoloration of colorants, loss of strength for textiles. Dust: disfiguration of objects; attractant for pests, scratching of soft surfaces by friction.
Pollutants transferred by contact	Material from storage, containers or showcases displayed with sulfur compounds, adhesives, PVC or polyurethanes. Fatty acids from people or from greasy objects such as skin/leather. Impregnation of salts during burial. Impregnation of residue of cleaning agents.	Discoloration of surface of the object in contact with harmful material from products or objects.
Intrinsic pollutants	Composite objects having compounds harmful for the other parts of the object, corrosion of copper in contact with leather (e.g. tanned leather object having copper parts), composite objects made of sulfur based compounds and metals.	Deterioration of the objects: acidification, discoloration or stain on objects. Secondary pollutant may speed up the degradation processes caused by oxygen, water vapor or other pollutants.

(Adapted from TÉTREAULT, Jean – Polluents…)

19.4.2. Physical factors and their effects

Physical factors act by direct or indirect (vibration induced movement) intervention such as impact, shock, vibration, pressure, and abrasion, resulting in imperceptible fissures, deformation, stress and pressure with large-scale effects, like the

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[420] HARVEY, Ronald; FREEDLAND, Cassia - Exhibition and Storage… p. 414.

complete rupture or collision of artifacts. Normally this type of degradation happens mostly by improper handling, transportation, storage or display.

For risk management purposes, physical factors are grouped into four categories according to their incidence and intensity[421]: i) catastrophic forces, which present a low incidence but a high intensity like earthquakes, war and vandalism, shipment disasters, extreme handling hazards, or building collapse; ii) working forces, with high incidence and moderate to high intensity, e.g., handling, transit, shipment, loads, construction vibrations; iii) cumulative forces, with high incidence and low intensity, such as handling objects over time, shipping with a poor packaging system, improperly designed supports leading to distortion or breakage after an extended period of time; iv) low-level forces, with variable incidence and low intensity, from vibrations caused by occupant activities, mechanical equipment, nearby road traffic and acoustic vibrations.

Besides these external forces, information about the preservation state, nature, weakness, geometry and flexibility of the objects is essential for understanding how hazards can be eliminated.

19.4.3. Other damaging factors

Other risks such as fire, water damage, theft and vandalism in collections must also be considered, providing strategies to prevent or minimize any occurrence. Fire and water damage can occur in heritage institutions, most of the time as a result of natural occurrences, technological hazards, mechanical failures or neglect. As for theft and vandalism they are considered a security matter, for which it is necessary to provide effective safeguard measures.

According to the type of damaging factor and the vulnerability of objects, so will be the damage, i.e. deterioration can range from a minor discoloration, distortion or dampness, respectively caused by a fire or flood for example, to total loss.

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[421] The intensity of physical factors can be seen in more detail in the work of MARCON, Paul – Ten Agents of Deterioration, Physical Forces…

19.4.4. Waterlogged organic materials and environmental factors

As mentioned, materials present singularities according to their nature and structure and this is important when choosing a treatment and also when preventing deterioration in storage or display.

The main cause of the degradation of leather is acid hydrolysis. As an airborne pollutant sulfur dioxide penetrates the leather surface, which beneath sunlight is converted into sulfur trioxide which, in turn, is absorbed by the leather tannins, where it is hydrated and converted into sulfuric acid, dissolving in the presence of moisture, producing hydronium H_3O^+, which can break the links between the polymer chains of amino acids. On the other hand, there are organic acids and breakdown products that can increase the quantity of hydrogen ions, thus increasing the potential for acid hydrolysis.

There are other sources of leather degradation such as perspiration. In this phenomenon the combination of moisture and heat leads to loss of phenols and under a high pH to perspiration and the darkening of the leather.

Chemical attack also deteriorates other animal materials such as wool or fur, with the most resistant being silk. Textiles made of silk appear to be quite resistant to acid hydrolysis, nevertheless, not so resistant to RH, temperature and light. Silk establishes strong bonds with water and due to this fact and considering that water acts as a plasticizer, when RH drop below 40%, desiccation occurs resulting in brittleness and rigidity[422]. Also, fluctuations in RH cause distortion of the silk fabrics, dimensional changes and fibers stress. As for temperature, besides encouraging a low RH with loss of water, it also results in thermal oxidation typified by yellowing of the fibers. In terms of photo-oxidation, silk is particularly susceptible to being damaged by UV, suffering a chain modification that will lead to bond breaking and weakening of the fibers with embrittlement and yellowing of the silk. The presence of other agents can also cause photochemical reactions that will derive in loss of flexibility. The thermal oxidation and the photo-oxidation serve to give an overall idea of the preservation state before the complex process of burial in waterlogged conditions takes place and also these features are particularly worrying when considering preventive conservation measures.

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[422] GARSIDE, Paul; WYETH, Paul – Textiles… p. 80.

The main alterations of cellulose-based materials are induced by RH. These materials are very sensitive to RH. If the RH is too high, fibers will absorb moisture and swell. If the RH is too low, in a first stage materials become brittle, followed by cell wall contraction, resulting in its structural distortion. If the RH tends to fluctuate distortions[423] and fractures of the fibers will occur.

Cellulosic materials are also deteriorated by photo-oxidation, acid hydrolysis, oxidation, and biodegradation. When exposed to light cellulosic materials suffer visible consequences of discoloration and general loss of strength. This phenomenon is due to the energy contained in UV radiation that produces the scission of the chemical bonds in the cellulose chain. The effects of acid hydrolysis on cellulosic fibers, show that especially the amorphous region is cleaved, indicating that hydrolysis does promote a degradation process, leading to the exposition of the cellulose and its degradation. Cellulose oxidation can be caused by a wide range of oxidizing agents and accelerated by the effect of alkaline pH and high temperatures[424]. No matter the type of agent, the result is always the modification of the structure, with shortening of the cellulose chain, and a weakening of the cellulose fibers.

As previously mentioned the environmental degradation of organic materials is related: in general all polymers and proteins are affected by light, temperature, moisture and pollutants and also affected by biological attack.

Concerning the waterlogged organic archaeological materials, the major issue after treatment is not only the materials themselves but also the deterioration and aging of the chemicals used for the stabilization of artifacts. Waterlogged objects will continue to suffer changes according to environmental factors, but also the bulking agents. For example, a wood treated with PEG is highly reactive to RH fluctuations, in an environment higher than 65% RH PEG dissolves leading to chemical and physical problems, such as an aesthetically sticky surface, the internal structure collapse[425] and also white spots, i.e., salt solutions that migrate from inside the wood to the surface, where precipitation takes place, leading to degradation[426].

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[423] Especially in wood materials due to their anisotropic character, and this means that they will shrink unequally according to their tangential, radial, and longitudinal directions.

[424] For further information about accelerated-aging and its effects on materials see FELLER, R. L. - Accelerated Aging Photochemical...

[425] GRATTAN, D. W. a) – A Practical Comparative Study of Treatments for Waterlogged Wood… p. 250.

[426] SANDSTRÖM, Magnus; [*et al.*] – *Op. cit.*

Another issue that affects these materials is carried out by visitors. Waterlogged archaeological materials have a mysterious aura that has the ability to transport visitors to another dimension: it is not just the historical and technological information they have, but probably the more interesting part is the story behind them. People are fascinated by objects that have survived under such conditions, and as a result maritime museums receive thousands of tourists every year. Excessive tourism has a negative effect on the museum environment, as an adult is able to release approximately 60 grams of water vapor per hour and 60 watts per square meter of body surface as heat affecting RH[427]. Thus, environmental conditions can fluctuate according to the number of visitors, as they release heat, water vapor as well as carbon dioxide. Also, tourists transport external solid particles, generate vibrations, along with other deterioration factors[428].

19.4.5. Display and storage, preserving waterlogged organic materials

Preventive conservation is regulated by prevention actions, monitoring and control. The planning, management, improvement and maintenance of waterlogged organic materials are no different from other collections. Thus, it must imply an interdisciplinary work articulated with the various technical areas involved in a museum.

Knowledge of the artifacts nature, characterization of the collections, inventory, classification of storage or exhibition spaces, environment measurement, description of the building and its construction, electricity, plumbing, internal and external artifacts circulation, explanation of human resources, allows the improvement of diagnostic tools, quantifying all risks, increasing the durability of conservation interventions and reducing costs, by determining an effective management policy.

For a long time 19-24°C and 45-55% RH, with seasonal fluctuations of 5% RH maximum, were seen as ideal conditions for the environment housing of organic objects[429]. Indeed the lower the temperature and RH, the lower the chemical degradation, thus a cold and dry environment is the optimal situation to preserve

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[427] CABELLO-BRIONES, C - A Reflection on the Preventive Conservation of Archaeological Wood … p. 45.

[428] *Idem*.

[429] THOMSON, Garry – *Op. cit*.

waterlogged organic materials. At least from a theoretical perspective, since these figures are not always achieved, due to the cost involved and also because collections usually include a variety of materials, thus a compromise must be found, always considering the most vulnerable and valuable item. It is more feasible to provide proper humidity values all year, regarding the equilibrium of the artifact to its surroundings, than trying to follow an unfeasible standard, especially considering the Portuguese climate and building conditions.

Temperature and humidity can be manipulated through proper equipment, and more susceptible objects preserved with ideal temperature and RH, by creating individual microenvironments through cases or rooms, either in storage or display.

To be able to maintain the required equilibrium, the environment must be characterized. It is essential to conduct periodic monitoring of temperature and humidity and subsequent data interpretation. Each room should be measured, as well as the objects surface, establishing if there is any exchange with the air or not[430]. To avoid reading errors, which can lead to inappropriate conservation actions, this procedure must be done with appropriate and calibrated instruments.

Because fungi, mould, insects and rodents can be the most damaging, biological growth must be prevented, which can be done through periodical inspections. Biocide or insecticide should be avoided since they have high toxicity.

Pollutants and light must also be measured, and reduced at the maximum. Outside air can be purified before it enters the museum environment and also a good ventilation system prevents solid particles and gaseous forms of pollution. This system must also minimize the internal effects produced by pollution from mass tourism and assorted materials used in the cultural units. In more critical situations reducing the entries of tourists can be a wise choice, along with avoiding materials that can release harmful vapors, like polyvinyl chloride (PVC).

Since waterlogged archaeological materials are very fragile, in order to protect items from physical damage, handling and transportation must be avoided. Also design procedures and performance data must be used when calculating display cases or storage containers.

Finally, in order to prevent artifacts and collections from being robbed, vandalized or to suffer from fire or floods, the global vulnerability of the collections

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[430] CAMUFFO, Dario; FERNICOLA, Vito – How to measure temperature and relative humidity… p. 39.

must be identified in order to address priority responses, according to each damaging factor and the objects. To eliminate these potential dangers, a management plan based on protection, detection, response and recovery must be implemented[431]. All staff must be aware of the possibility of any of these incidents, minimizing risks.

20. Discussion

As mentioned, recognizing the chemical and mechanical forms of deterioration will help to identify the conservation needs of an artifact. Because materials are quite complete, analyses are important to provide a better understanding of the rates and nature of deterioration. This information will help to develop an *in situ* preservation methodology and a treatment strategy, from the rising to the exhibition or storage.

The major issue in treatment of waterlogged archaeological organic materials is their stabilization, however depending on the nature, state of preservation and future use, different methods of impregnation or bulking can be used.

Since their implementation, silicone oils have been proven to have good results with low maintenance. However, despite the amount of time this implies and the preventive conservation issues, the most used method of impregnation is still PEG, with two different molecular weights. Sucrose and acetone-rosin are also good choices, easy to perform, although they cannot be used in every organic material. Freeze-drying can also be used, either as a singular drying treatment or as part of PEG treatment, but small shrinkage cannot be avoided. Supercritical drying is still a new procedure, apparently with good results, nevertheless, the degree of technical requirement, the equipment needed and its cost is still a handicap.

In Portugal, the method used to treat waterlogged wood is PEG. The woods from the *Ria de Aveiro A* have been impregnated with PEG with two different molecular weights 400 and 4000, i.e. a two-step treatment, followed by control drying. However, after 8 years of treatment it is still not concluded, and the forecast for its completion is over 20 months. Concerning the exhibition of the *Ria de Aveiro* hull there are no

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[431] An introduction to security risk management, based on concepts developed by the Royal Canadian Mounted Police and the Government of Canada Security Policy is given by TREMAIN, David - Ten Agents of Deterioration, Thieves and Vandals…

predictions, but due to the PEG environmental needs and considering the Portuguese climate, a special room must be provided for either display or storage.

Considering the amount of underwater archaeological sites, their organic contents, the amount of artifacts that are still waiting to be treated in the DANS, we think that the best preservation option will be the introduction of new methods such as *in situ* preservation, *in situ* storage and for treatments, silicone oils.

Also, in a climate zone such as Portugal divided into two regions, the north with wet winters and moderately hot in the summer, the south with a temperate climate with wet winters and hot dry summers[432] and assuming that properly heated and non-humidified buildings do not exist, it appears that, despite some damage, many objects have survived in museums. Nonetheless, this is a general observation across whole categories of materials, verified over professional years. The major concern is the response of treatments and their bulking materials to temperature and RH, especially this last one, and its effects upon artifacts.

Artifacts and environment are seen as a continuous system, where a timely diagnostic plays the major role, increasing the durability of conservation treatments, optimizing actions and decreasing maintenance costs. Preventive conservation is considered a responsibility that depends on daily strategies, based on environmental monitoring and disaster planning. These procedures should be adapted to each material and necessarily combined with preservation and maintenance activities.

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[432] INSTITUTO DE METEOROLOGIA - Normais Climatológicas…

CHAPTER V – CASE STUDIES

The conservation of waterlogged organic materials is complex, involving several actions, the most challenging being the artifacts stabilization, minimizing the shrinkage or collapse of the structures. Considering this feature several compounds and methods have been studied and used for treatments of waterlogged organic materials. Since the focus of this thesis relies on the presentation of the best procedures for the conservation of underwater organic artifacts collections, in order to attain more information about conservation treatments several conservation treatments were developed. The first study concerned the removal of iron stains, since this is one of the most difficult conservation tasks. The second and third were based on a silicone oil impregnation, whereby we attempted to attain more information concerning the steps of the conservation treatment, as well as to perceive the silicone impregnation ability. Finally, in the last we performed an experiment to promote the extraction of alkoxysilanes from treated waterlogged archaeological wood.

21. Methods for the removal of iron stains from cellulosic fabrics

21.1. Objectives and research plans

Considering the high possibility of waterlogged archaeological organic materials presenting iron oxide stains and also considering the severe chemical effects of those on the artifacts, along with the misrepresentation of the surface aspects, it is essential to understand the extent and feasibility of treatments. For this purpose, an experiment was conducted revealing a simple method for the removal of iron oxides from cellulosic material. In this experiment the methods used were based on the Canadian Conservation Institute (CCI) cleaning procedures.

The CCI treatment was specially developed to be applied to leather and leather related materials[433]. Nevertheless, considering the nature of the stains, the chemicals used and the method itself, we believe that it could also work on cellulosic textiles.

The orange-red color stains present a problem for conservators, since these stains are iron in its ferric state (Fe III) which is not easily soluble in water[434]. For this

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[433] LAFRANCE, Jessica - Efficiency and quality in a bath treatment …

[434] SELWYN, L., S. Tse, - The chemistry of sodium dithionite...

reason, the treatment for removing iron stains from cellulosic fabrics requires a two-step procedure. First, it is necessary to oxidize the ferric iron (Fe III) into ferrous (Fe II), which is accomplished through a reducing agent. The second phase of the procedure consists of removing the Fe (II) produced by the reduction process[435], with it being necessary to use a chelating agent. This chelating will retain Fe (II) molecules in the water, which are then easily removable through rising. If this agent is not used FE (II) oxidize back into FE (III) forming a new stain[436].

In this experiment we used sodium dithionite as a reducing agent[437] and EDTA[438] and dibasic ammonium citrate as chelating agents[439].

21.2. Materials and methods

An iron-stained cotton master piece was divided into five samples (3,2 x 2 cm) (Fig. 18) and each labeled with the treatment name: A, for dibasic ammonium citrate (2% w/v); B, EDTA (2% w/v) and sodium dithionite (5% w/v) in a proportion 1:1; D, for sodium dithionite (5% w/v); and E, for EDTA (2% w/v). Sample C (Control), did not receive any kind of treatment, it was used only to compare the effects of the performed treatments.

Samples A, B, D and E were placed in the disposable Petri dish, and 15 ml of the specific treatment was applied; for example, the sample in the Petri dish labeled A, received only the treatment of the dibasic ammonium citrate (2% w/v) and so on. The Petri dishes were covered, and the time counted was 15 minutes at the most. During that period, samples B and D immediately started to react and color changing was observed.

After 15 minutes, the samples were rinsed in running tap water for 15 minutes more. Samples were then placed between multiple sheets of blotting paper and the excess of water removed. At the same time pressure was applied to avoid the formation of wrinkles that normally occur during the drying phase. Finally, after drying, samples were transferred to polyethylene bags.

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[435] *Idem*.

[436] SURYAWANSHI, D.G., BISARIA, S. K. -Removing Metallic stains…

[437] LAFRANCE, Jessica - Efficiency and quality in a bath treatment …

[438] RABIN, P.M.- A Study of Iron Stain Removal …

[439] MACLEOD, I.; [*et al.*] - Observations on the extraction of iron and chloride…; GODFREY, I.; [*et al.*] - Iron Removal from Waterlogged Leather and Rope ; MARDIKIAN, P; [*et al.*] - A Preliminary Investigation into the Effects of Diammonium Citrate…

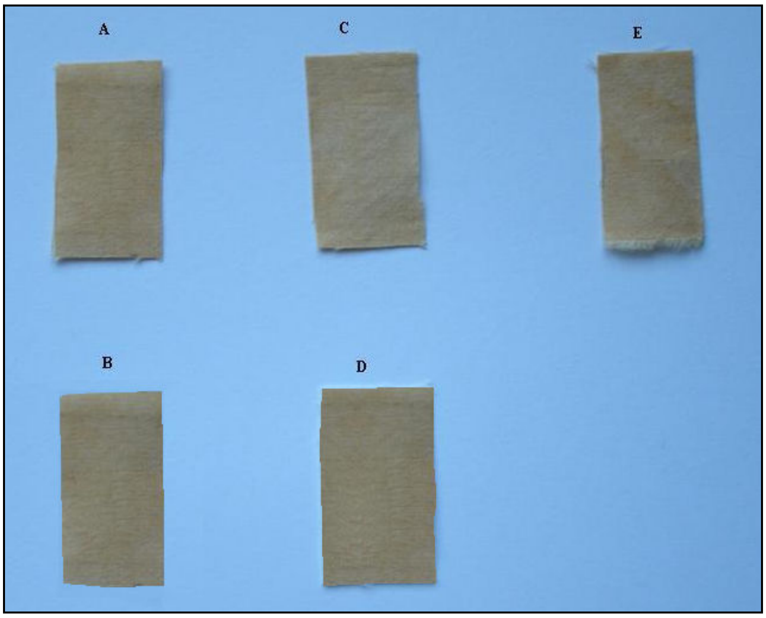

Figure 18 – Aspect of the cotton tissues before treatments.

21.3. Results and discussion

Analyzing the results and compared with sample C we verify two different reaction groups: one with no alteration in the removal iron stain, which includes samples A and E; and the other group, presenting good results in the elimination of iron stains, such as samples B and D.

The solutions applied to samples A and E are chelating agents[440]. The maintained iron stain on these samples proves that chelating agents only work, when they have Fe (II) available. They do not have the ability to sequester the insoluble Fe (III).

Samples B and D presented the best test results (Fig. 19). In sample B, the applied solution has reducing and chelating ability[441]. The sodium dithionite in water reacts and produces sodium bisulfite and sodium bisulfate[442]. The sodium bisulfate reduces the insoluble iron Fe (III) into a water soluble form Fe (II). This amount of Fe (II) is inactivated by the EDTA[443], since this chelating sequesters and eliminates the Fe

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[440] LAFRANCE, Jessica - Efficiency and quality in a bath treatment …
[441] SURYAWANSHI, D.G., BISARIA, S. K. -Removing Metallic stains…
[442] IRWIN, Seth - A Comparison of the use of sodium Metabisulfite and Sodium Dithionite…
[443] LAFRANCE, Jessica - Efficiency and quality in a bath treatment …

(II) capacity to react with other elements or ions, avoiding the possibility of forming a new stain. Sample B was the quickest and most effective for iron stains elimination.

The solution applied to sample D presented a high capacity to reduce Fe (III) into Fe (II). Nevertheless, without an application of a chelating agent the risk of residual Fe (II) being left in the sample is enormous over a long period of time. In this case Fe (II) will eventually oxidize back into Fe (III) producing a new iron stain[444].

In this experiment, the use of stronger and more hazardous chemicals were avoided. Thus, the use of this solution is strongly recommended providing that safety rules are properly followed: gloves, eye protection, masks and, if possible, carrying out the work in a ventilated room.

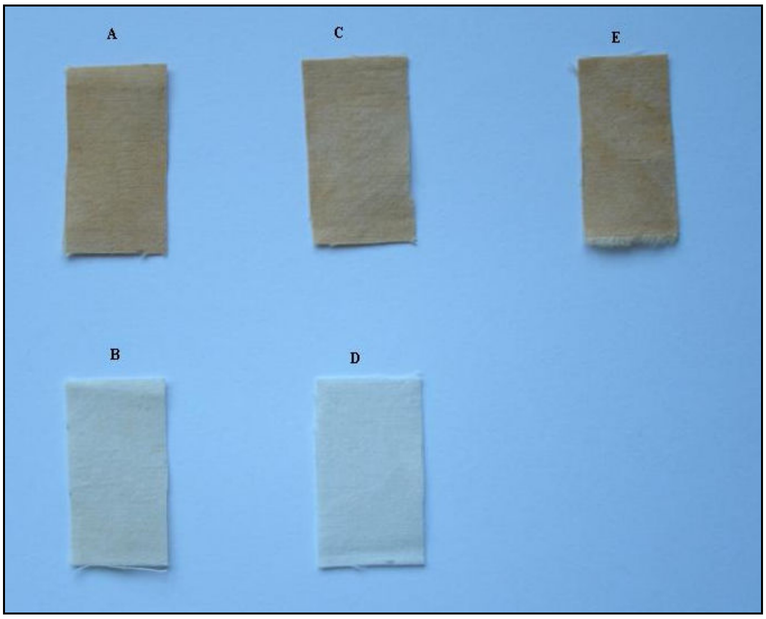

Figure 19 – The cotton tissues after iron removal treatment.

22. Silicone oil

Silicone oil is being used as a consolidator for organic (and inorganic) materials. Considering its effectiveness and the goals of this research, it is important to synthesize and characterize the silicone method, as a chemical that is able to maintain the aesthetic, mechanical and physical characteristics of artifacts, with great durability and stability.

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[444] IRWIN, Seth - A Comparison of the use of sodium Metabisulfite and Sodium Dithionite…

For this purpose, several shoes and shoe parts were conserved, in one of the most recognized conservation laboratories for silicone treatments, the Conservation Research Laboratory (CRL) in Texas A&M University (TAMU).

The main objective of those studies was to understand the extent of the bonding between wood and silicone, by impregnating new wood with this chemical and analyzing the expansion of that impregnation and to proceed with the removal of silicone oils from several artifacts treated ten years ago at the Archaeological Preservation Research Laboratory (APRL) at TAMU.

Ideally, the materials used to consolidate or to stabilize archaeological artifacts should be able to be removed without constraints. However, silicone is known for its ability to create a homogeneous union with materials, changing its structure composition. Despite this feature, investigations concerning the removal of silicone oils from several artifacts treated ten years ago, at the Archaeological Preservation Research Laboratory (APRL) at TAM, were carried out. The main objective of this experiment was to understand the effects of this action upon the materials structure.

22.1. *Paços do Concelho Palmela's* shoes conservation procedure

22.1.1. The *Paços do Concelho Palmela* archaeological excavation

The seventeenth-century *Paços do Concelho* building, in Palmela, has in its history, had several functions over the centuries: court, jail, butcher and carriage repair workshop, just to mention a few. From an architectural point of view it is a building which is emblazoned (it has the coat of arms of the town of Palmela) and consists of two floors, which survived despite some damage caused by two earthquakes in 1755 and 1858[445]. In the beginning of the XX century it was assigned to the National Guard and later, in 1926, it became the City Hall. Subsequently, at that time there were a series of improvements and architectural changes in the building with radical transformations, from open store spaces into offices[446].

The archaeological investigations undertaken in this building began in 1992, in the west part of the building. It consisted in the archaeological study of a barrier, resulting from the demolition of two existing dwellings. The stratigraphic record

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[445] FORTUNA, A. Matos – Monografia de Palmela...

[446] *Idem.*

allowed the identification of twenty-six units with archaeological contexts that fit between the end of the XIV century and the XIX century. One of the identifying contexts was a well, but this was not excavated until 2007.

In 2007, the archaeological investigation in *Paços do Concelho Palmela* building was resumed and the well was excavated. It was interpreted as a dump where brown earth mixed with gray-green clay was present; followed by lime, yellow mortar with small and medium stones (limestone and sandstone) and several fragments of brick.

Sediment found inside the well (stratigraphic unity 5A) was very similar to the previous, but with a darker shade. Also, abundant pottery fragments of common glazed pottery, metallic elements (iron, bronze), of which a buckle, a projectile cannon, a lock, mammalogical and malacological fauna were identified. A red pot with a dark surface was also found, along with kaolin pipes and a stoneware bottle with an inscription: WYNAND FOCKINK AMSTERDAM, all dated from the XVIII-XIX centuries.

The next unit (stratigraphic unity 5B) showed abundant food debris, such as various burned bones, seeds and pine cones, roots, branches or arms of some vine that may correspond to the remains of pruning or must, deposited inside the well during their (re) use as the site for disposal of waste. The percentage of glazed ceramic and porcelain is smaller, with common ceramics predominating. The presence of abundant charcoal, burnt bones and pottery with blackened surfaces and soot, the changed tone of the sediment and the black pit walls that arise, suggest that a fire occurred inside the well. Fragments of French roof tiles were observed, some of them presenting white and yellow paint. A ceramic figure of a Christmas crib from the XIX century was also found. At this level of deposition the presence was recorded of a cobbler mold, sticks, strips of leather, and shoe soles, which were removed.

The last unit (stratigraphic unity 5C) with very black and greasy sediment was flooded. In there was found a high percentage of debris, leather, soles, shoe form (last), shoe-repair tools, branches, shoes and coals. The presence of ceramic vessels was greatly reduced. A lot of clam shells and charred pine cones were collected.

The excavation of the last two levels was reported by the entire archaeological team as being very complicated, due to the water and smell, leading to situations of malaise and irritability of the respiratory tract.

Despite the influence of post-depositional phenomena found in the 5B level, it is possible to indicate the XVII-XVIII centuries (Modern Period) as the time line for the shoes, cobbler mold, sticks, strips of leather and shoe soles. They seem to come from the context of a shoemaker's workshop, where the waste had been deposited into the well.

22.1.2. First examination and choice of treatment

After being removed from their archaeological context the materials were placed in polyethylene bags and containers and their preservation state identified by the archaeology team. The majority of organic artifacts recovered from the well of *Paços do Concelho,* although wet or soaked, were considered to be in a medium or bad preservation state. Despite this analysis the objects did not receive any treatment, remaining in the same bags or boxes for two years, with little water in them. Twice a year the materials were checked and if water was found to have evaporated, new tap water was introduced.

In 2009 it was decided that these artifacts would be in an exhibition, and due to the need for conserving the artifacts the author of this thesis was contacted to perform the required treatment.

After a general analysis, the preservation state was considered to be very poor. The collection was divided into two, the ones that were dry, with white spots, mould and completely disintegrated; and the rest with some humidity, fragility, white spots, also presenting signs of salts and evident collapse. Due to this circumstance they were not displayed and only three of the ones that still appeared with some humidity chosen to be conserved. Those chosen were: a wooden last, a lady's shoe (mule), a men's shoe (desert boot) and child's shoe parts.

These artifacts represented a challenge to conservation and so, treatment by silicone oils method was considered the best option. The idea was to integrate this treatment as a case study to be presented in this thesis (which was already assumed as an investigation into the silicone conservation method) as an example of the ability of treatments with silicone in extremely decomposed waterlogged organic materials which were almost dried, and how these methods could be used by archaeology and conservation in Portugal.

The conservation treatment was defined in conjunction with Prof. Donny L. Hamilton at the Anthropology Department in TAMU, and the work carried out at the CRL with Helen Dewolf�given's assistance, from September to December, 2009.

22.1.3. Pre-treatment documentation and diagnostic

As mentioned before (Chapter IV of this work) any intervention artifacts must be carefully examined and recorded. When the transportation plastic bags and containers were opened, objects were removed and photographed (Fig. 20-22). Artifacts were identified as wood and leather. All of them were damaged and covered with heavy mud and other elements matrix with a slight humidity; also presented white spots; very dark colors and a strong smell was also detected in all items. The wood presented a spongy feeling, which was inferred as destruction of the cell wall structure. As for the leather it showed signs of oxidation and resembled gelatin, which means high hydration of the protein.

Chemical analyses were not performed, however, as due to the archaeological context (well with sediment and water) and physical characteristics the existence of an enzymatic process of biotic agents (fungi and bacteria) was believed to be a part of the degradation process. The white spots were not considered the effects of biological attack, rather salts that had come out of materials due to wet and dry cycles.

Considering all these features the artifacts were diagnosed as heavily degraded.

Figure 20 –Aspect of the desert boot before treatment.

Figure 21 – Aspect of the mule before treatment.

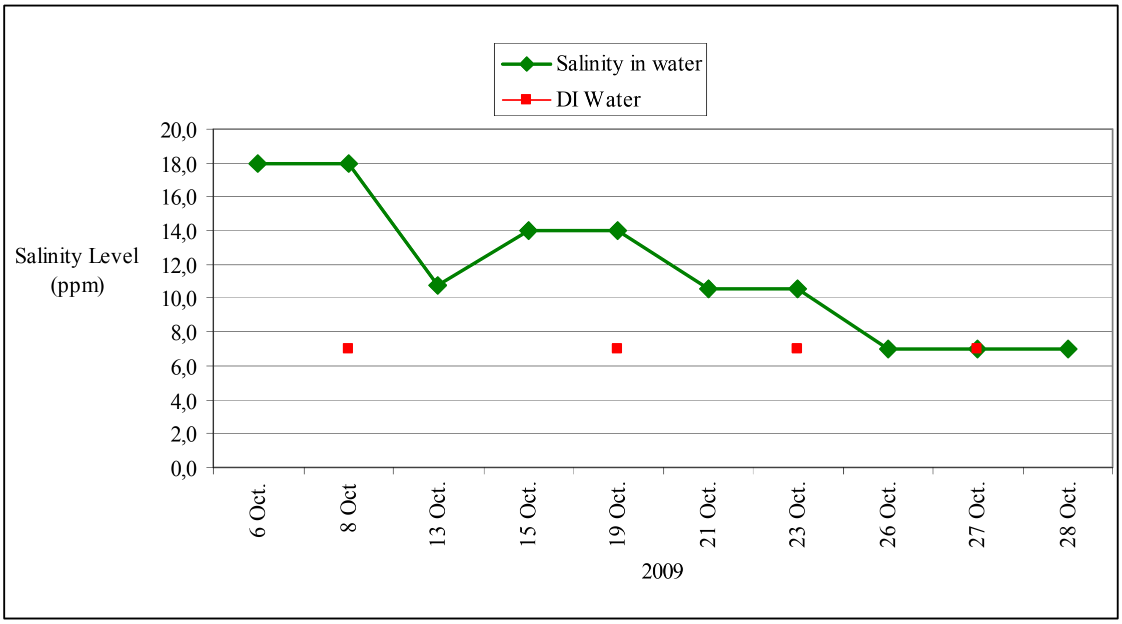
Figure 22 – Aspect of the wood last before treatment.

22.1.4. Silicone treatment procedure

The process used to conserve the *Paços do Concelho Palmela* artifacts was the silicone oil method used by the CRL, (see Chapter IV of this thesis) which is synthesized by: desalination, dehydration, impregnation, cleaning, and catalysis.

Due to the lack of time and considering that the artifacts were almost dried, to start with the desalination process, they were immediately immersed in reverse osmosis water. After reaching a low level of salts, DI water was used until the concentrations of salts were less than 7 ppm of chloride (Graphic 1). While performing the desalination a first cleaning could have been done, however due to their preservation state and to avoid causing even more degradation, it was decided not to clean the artifacts before the silicone impregnation and consolidation.

Graphic 1 – Desalination Treatment of the wooden last, desert boot, mule and child's shoe parts.



To extract water from the artifacts they were all immersed in nine solvent baths of ethanol and acetone. To avoid osmotic pressure, dehydration was progressive starting with 75% water and 25% ethanol. Every week, the objects were placed in a new bath with 25% increments until 100% of ethanol was achieved. By that time baths had changed to a mixture of ethanol and acetone that began with 75% ethanol and 25% acetone. Again, they were changed every week with increases of 25% of acetone until 100% acetone was accomplished. To complete the process, the materials were immersed for two days in a last bath of 100% fresh acetone.

After being completely dehydrated by the solvents, the artifacts were removed from the acetone bath and directly submerged in a solution of 100% of low viscosity silicone oil (Fig. 23), the SFD1 (~75 cSt) to which was added 20% of methyltrimethoxysil and (MTMS) cross-linker.

Due to the small size of the artifacts they were able to stay in small containers which allowed using a vacuum chamber, enabling a faster exchange of acetone and polymer, thus a better impregnation. The vacuum impregnation took a week to be completed. It began with a slight vacuum which was gradually increased around approximately 25 in Hg gauge. During this stage small bubbles were seen leaving the object, first a considerable amount, followed by just a few by the end of impregnation.

Figure 23 –Aspect of the mule when submerged in silicone oil treatment.

To conclude the impregnation and because the vacuum chamber could not be opened suddenly, otherwise the materials could experience collapse, for 5 days the vacuum was gradually decreased. Finally, after this period the materials were allowed to stay at ambient pressure for a period of 48 hours.

The artifacts were then removed and allowed to drip dry for another week. By the end of it, in order to remove the excess of silicone and to obtain a more natural appearance, mechanical and chemical cleaning was carried out. Throughout this stage all elements were taken apart, allowing a better analysis of each artifact. The mule was dismantled in its thirteen pieces: seven belonging to the heel; one outsole; two midsoles; a shank; one insole; one vamp. This allowed the identification of traces of nails that held the pieces all together, and some other elements that were inside this shoe, such as leather straps and an olive pit. The shoe was also taken apart into: midsole; foothill; vamp; and tongue. Inside this shoe other elements were found: one child’s midsole; a child’s outsole with two flat bottom rear parts; one shank; one midsole with a shank; a small piece of glass, and a fragment of ceramic.

During the mechanical cleaning the remaining mud was removed, along with the iron oxides in the soles and the other elements that were attached or inside the shoes. To remove these items dental picks and forceps were used to scratch inside the shoes. For the chemical cleaning swabs, brushes and paper towels impregnated with pure MTMS were used. After the cleaning was completed, the mule was assembled with dark fiber glass in the holes of the iron nails and sewed with nylon line, which was painted back at the end of the work.

The final step of this treatment was to join permanently the polymer molecules, ensuring their stability. This was achieved by placing some of the artifacts in a sealed plastic container along with a fresh catalyst dibutylin diacetate (DBTDA). The mule remained for two periods of five days each; the child's shoe parts and the other small pieces went to catalyst for four days. After being catalyzed the artifacts received a final mechanical cleaning which intended to remove any catalyst left, this was attained by placing all objects in a fume hood for 48 hours. The last and the men's shoe were not catalyzed.

22.1.5. Results and discussion

The silicone method is simple to plan and to perform, it does not require especial instruments to be developed and good results are easy to attend. All the artifacts presented good mechanical strength, with a good dry and natural texture (Fig. 24-26). With the aesthetic feature most depending on the preservation state.

Figure 24 – Desert boot after the silicone oil treatment.

Figure 25 – Aspect of the mule after the silicone oil treatment.

Figure 26 – Wood last after the silicone oil treatment.

Despite using solvents to extract water from the materials, and considering the effects of acetone in leather components, apparently this dehydration did not harm the structure of proteins, or the wood polymer.

However, the catalyst appeared to have more secondary effects. Thus, the materials that went for a longer time in to catalyst became very stiff, especially the vamp of the mule; followed by the child's shoe parts and middle soles that suffered for a shorter time the effect of the catalyst. On the other hand, the wood of the last and the shoe that did not pass by the catalyst still remained soft. Therefore, the author considers the last part of the silicone method the one that requires most attention.

As a final conclusion, for badly preserved organic objects, silicone treatments do seem to present great results at a mechanical and aesthetic level.

22.2. Silicone oil treatment, impregnation of non-degraded wood

22.2.1. Objectives and research plans

Considering that the depth of impregnation depends not only on materials proprieties, but also on the consolidant properties and the method of the impregnation process. Thus, to better understand the ability of silicone polymers to saturate organic materials, samples of three types of wood (pine, oak and elm) were impregnated with two different silicone oils, one with more viscosity than the other. As for the impregnation method, impregnation under pressure was chosen, since the immersion of materials in a liquid submitted to a decrease in pressure efficiently enables the removal of gas from the pores, replacing it with the chosen consolidant[447].

This experiment was conducted on new wood, with no degradation of the cell walls, once we considered that only by using new materials was it possible to truly understand the extent of silicone oil penetration. The chosen species were: Pinus *taeda* L., known as Loblolly Pine, one of the most commercial woods in the United States of America, and very similar to *Pinus pinaster Aiton*, used in Portugal for the construction of ships; Quercus *alba* L. or White Oak, that presents related mechanical characteristics with Quercus *faginea* L.; *Ulmus spp.,* also a hardwood, chosen just for its resistance, normally used in the construction of military equipment.

After impregnation the wood samples were macro and micro analyzed, identifying the most and the least impregnated, according to the wood type, physical and aesthetic features. The effectiveness of impregnation also placed focus on the molecular weight of the silicone used when compared with control samples (without silicone oil impregnation).

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[447] KOTLIK, Petr – Impregnation under Low Pressure… p. 43.

22.2.2. Materials and methods

The experiment began by identifying, measuring and weighing all the wood samples (pine, oak, and elm). Samples were named according to the species and future polymer impregnation with Q1-3563 (Xiameter® PMX-0156 Silicone Fluid) and SFD-5 (Xiameter® PMX-200 Silicone Fluid): Pine Control; Pine Q1-3563; Pine SFD-5; Oak Control; Oak Q1-3563; Oak SFD-5; Elm Control; Elm Q1-3563; and Elm SFD-5.

After documentation, samples were hydrated by placing them in a sealed container full of deionized water for one week. At the beginning of the hydration process, samples had a tendency to float. To assure their immersion, a plastic mesh and some weights were placed on the samples. At the end of the week, the mesh and weights were removed and none of the samples were floating, meaning that impregnation had succeeded well.

Samples were then submitted to dehydration baths of 24 hours each, according to the method developed in CRL and APRL (see Chapter IV). Starting with a solution of 75% of DI water and 25% ethanol (v/v), followed by another with 50% of DI water and 50% ethanol. The third solution applied was composed of 25% of DI water and 75% ethanol (v/v), and a last bath 100% of ethanol. For the next phase of dehydration the process followed the same sequence and timing for baths, but only ethanol with acetone was used.

Completing the forced dehydration process, one third of the samples were impregnated with silicone Q1-3563(Xiameter® PMX-0156 silicone fluid), and another third saturated with SFD-5 silicone oil (Xiameter® PMX-200 silicone fluid). The differences between the two silicones rely on the viscosity; the Q1-3563 silicone has a low viscosity (72 cSt) and SFD-5 a high viscosity (12.500 cSt).

The impregnation began by a quick transfer from the last bath of the acetone (100%) to a container with its correspondent mixture (Q1-3563 and SFD-5) of 85% silicone oil and 15% of MTMS (v/v), and placed in a vacuum chamber.

In the vacuum chamber samples were submitted to sequences of pressures, measured in vacuum gauge pressure, beginning with a low vacuum value, which was progressively increased. The pressure started at 12 Inches Hg for 30 minutes; followed by 16 Inches Hg for more than 30 minutes. After this time, the vacuum was increased to 18 Inches Hg and kept for 48 hours. Finally, reaching a vacuum maximum value of 22

Inches Hg, for 24 hours, after which the vacuum was gradually reduced, until an ambient pressure was achieved, and maintained for 24 hours.

Samples were then placed in a mesh to drain the excess of the mixture (SFD-5+MTMS/Q1-3563+MTMS) for a minimum of 48 hours. To complete the process, the surface samples were cleaned with swabs impregnated with MTMS.

To retain the silicone oil in the samples a catalyst was used, the DBTDA. For this purpose, samples Q1-3563 and SFD-5 were sealed in different plastic bags with 15 g of DBTDA each, and placed in a fume hood for 24 hour.

In the last part of this experiment, all samples were transported to the St. Joseph's Medical Center, where a Computer Tomographic scanning (CT scan) was done. This exam allowed the visualization of the effects of the treatments in the different wood samples. The CT scan images were used to analyze the evolution of the Q1-3563 and SFD-5 penetration into the cell tissue.

22.2.3. Results

To better visualize the results, the data are presented into two categories, macro and microanalysis. The first was performed by an examination of colors, analyzed through the Munsell® Soil Color Chart (Munsell 1946) and by identification of the differences in mass, length and width/diameter. The second was based on the analysis of each wood CT scan images.

22.2.3.1. Pinus *taeda* L., Loblolly Pine from southern US

22.2.3.1.1. Macroanalysis

A smooth changed color between the samples with Q1-3563, SDF-5 (silicone oil) and Control on the Loblolly Pine dowel observing was observed (Fig. 27). The Control presented a natural color because it had not received any treatment, but the samples Q1-3563 and SDF-5 appeared to have a very pale brown color (10YR 8/4 by Munsell reference colors).

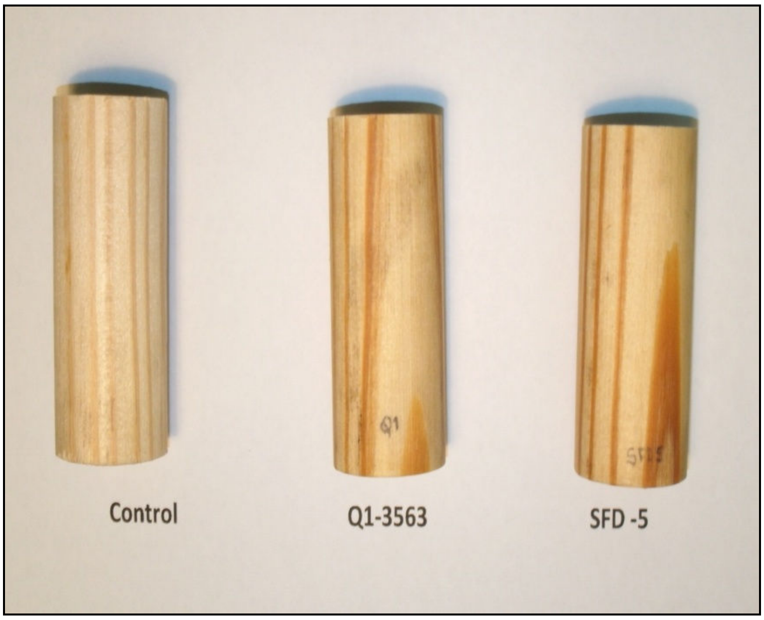

Figure 27 – Aspect of the Loblolly Pine Dowel with Control, Q1-3563 and SFD-5 treatment.

On parameter mass, length and width/diameter (Table 5), it was observed that the Q1-3563 sample had an increase of the mass content in 10.3% and SFD-5 had only 9.8%. This can be explained by the original mass density of the pine wood 500 Kgm^{-3}, as a medium capacity to retain silicone oils.

Wood cannot expand too much in a longitudinal way (length) because it is composed of a fiber tissue. In this case Loblolly Pine treated with SFD-5 expanded only 0.5% and 0.4% for the Q1-3563. These differences are minimal.

As for the width/diameter, a small increase of this parameter for the sample SFD-5 in 1.2% and 0.9% on the Q1-3563 was observed.

Table 5 – Data of the Loblolly Pine Dowel before and after application of the silicone oils.

	Pine (dowel cylinder)								
	Mass (g)			**Length (cm)**			**Width/diameter (cm)**		
Treatment	**Before**	**After**	**Change (%)**	**Before**	**After**	**Change (%)**	**Before**	**After**	**Change (%)**
Control	31.90	31.90	0.00	7.45	7.45	0.00	3.26	3.26	0.00
Q1-3563	32.03	35.70	10.30	7.30	7.33	0.40	3.26	3.29	0.90
SFD-5	31.39	34.8	9.80	7.35	7.39	0.50	3.26	3.30	1.20

22.2.3.1.2. Microanalysis

The scanning image (Fig. 28-30) shows the intensity and presence of the red marks for treatments Q1-3563 and SFD-5, both presenting notable differences between the two silicones. Silicone Q1-3563 has the minor viscosity, and passes better through the cells of the Pine dowel (soft wood) rather than SFD-5 treatment.

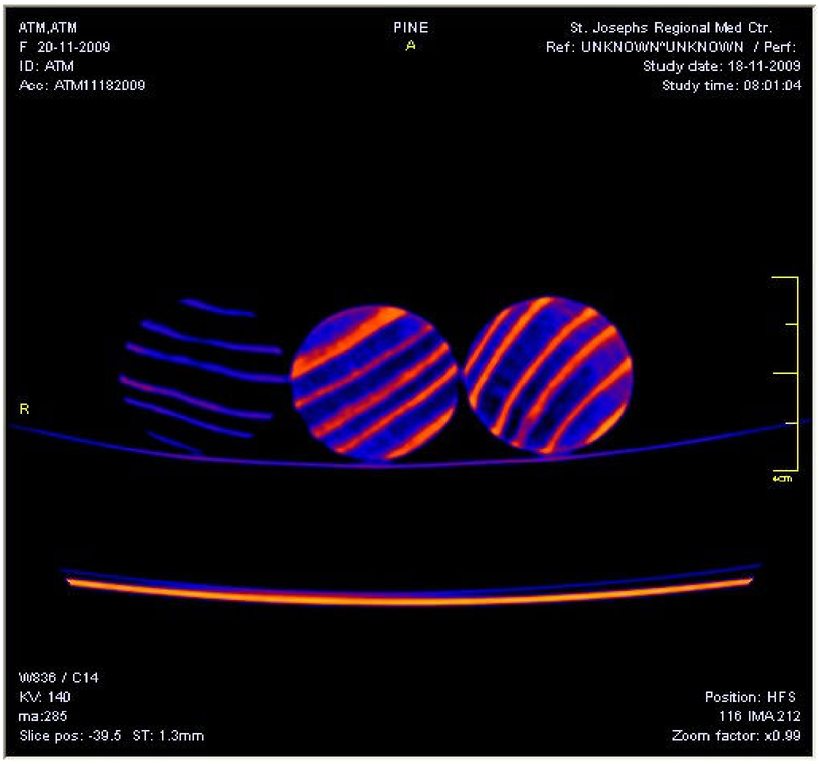

Figure 28 - CT scan of the impregnation process in Loblolly Pine dowel (KV:140; ma: 285; Slice -39.5; original zoom factor: 0.99).

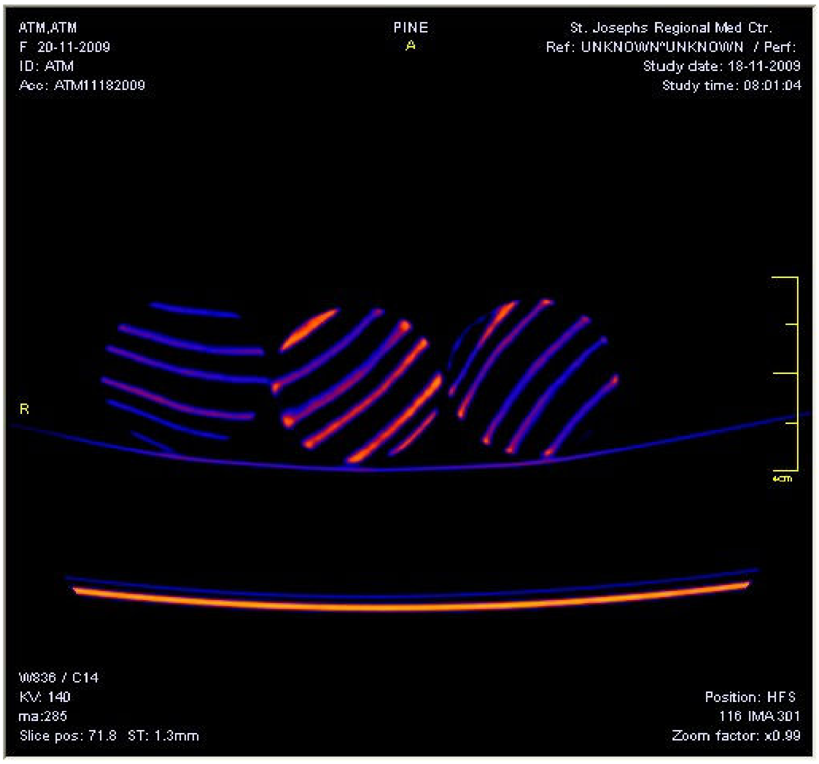

Figure 29 - CT Scan of the impregnation process in Loblolly Pine Dowel (KV:140; ma: 285; Slice 71.8; original zoom factor: 0.99).

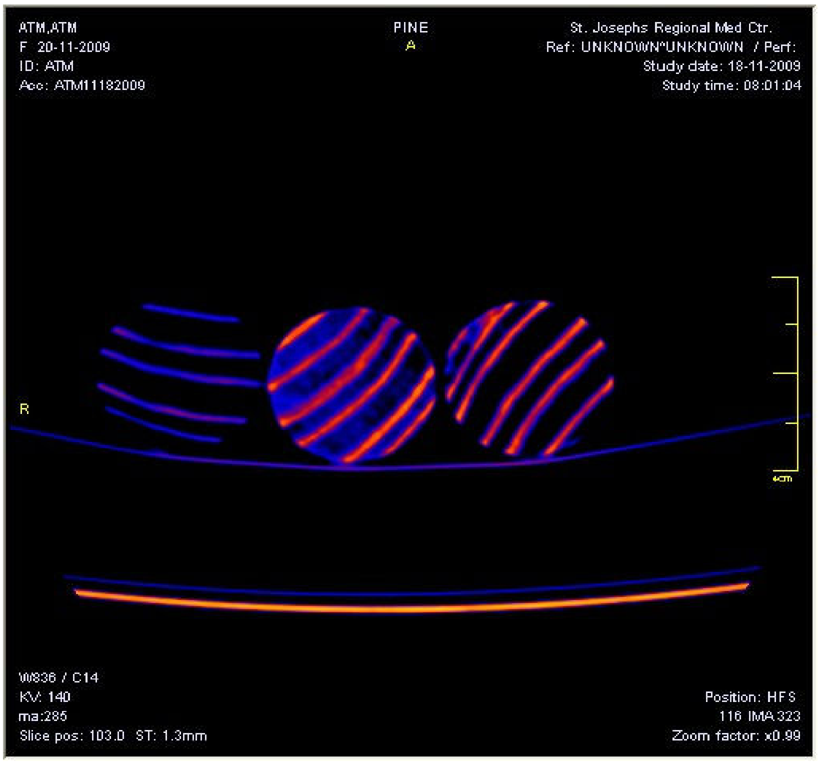

Figure 30 - CT scan of the impregnation process in Loblolly Pine Dowel (KV:140; ma: 285; Slice 103.0; original zoom factor: 0.99).

22.2.3.2. Quercus *alba* L., White Oak from eastern North America

22.2.3.2.1. Macroanalysis

Analyzing samples of the different treatments in the White Oak dowel (Fig. 31), it is confirmed that the wood with Q1-3563 and SDF-5 presented a brownish yellow color (10YR 6/6 by Munsell reference colors), different from the Control.

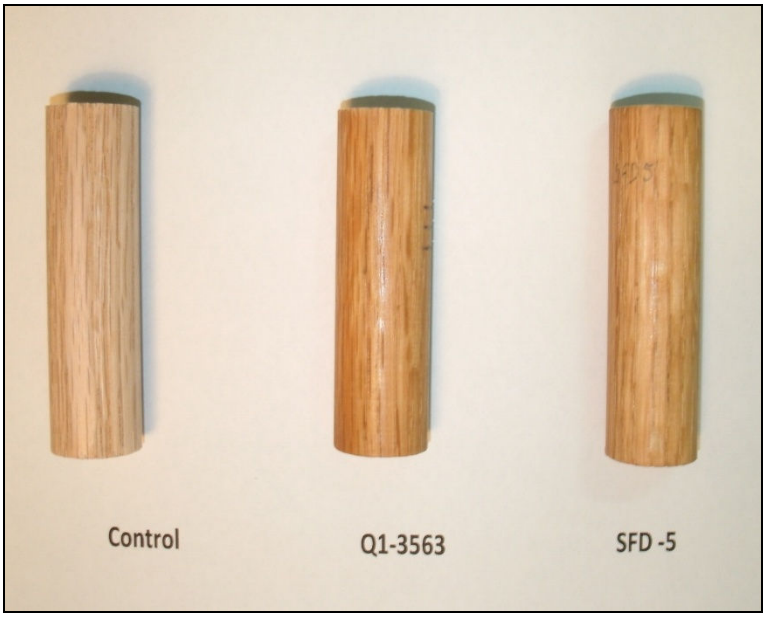

Figure 31 – Aspect of the White Oak Dowel with Control, Q1-3563 and SFD-5 treatment.

The Mass parameter (Table 6) of Q1-3563 treatment increased the White Oak in 11.8% and SFD-5 only 11.0% of the Oak mass. It means that this wood is able to retain much more silicone oil (Q1-3563, SFD-5) in its cells. This is due to the high level of fibrous tissues and micro pores, presenting a mass density of 640 kgm^{-3}.

Analyzing the length of the White Oak dowels, we observe that Q1-3563 treatment increased this factor in 1.9% and 1.1% for the SFD-5 treatment. Once again the differences between them are not significant.

In the width/diameter factor, an increase in the Oak dowel with the Q1-3563 in 2.3% and 1.2% on the sample SFD-5 was confirmed.

Table 6 – Data of the White Oak Dowel before and after application of the silicone oil.

Oak (dowel cylinder)									
	Mass (g)			Length (cm)			Width/Diameter (cm)		
Treatment	**Before**	**After**	**Change (%)**	**Before**	**After**	**Change (%)**	**Before**	**After**	**Change (%)**
Control	26.30	26.30	0.00	7.28	7.28	0.00	2.55	2.55	0.00
Q1-3563	25.92	29.40	11.80	7.23	7.37	1.90	2.55	2.61	2.30
SFD-5	25.89	29.10	11.00	7.18	7.26	1.10	2.55	2.58	1.20

22.2.3.2.2. Microanalysis

Observing the CT scan images of the White Oak dowels it is possible to verify, through the red markers, that Q1-3563 and SFD-5 penetration into the cell tissue is practically the same (Fig. 32- 34).

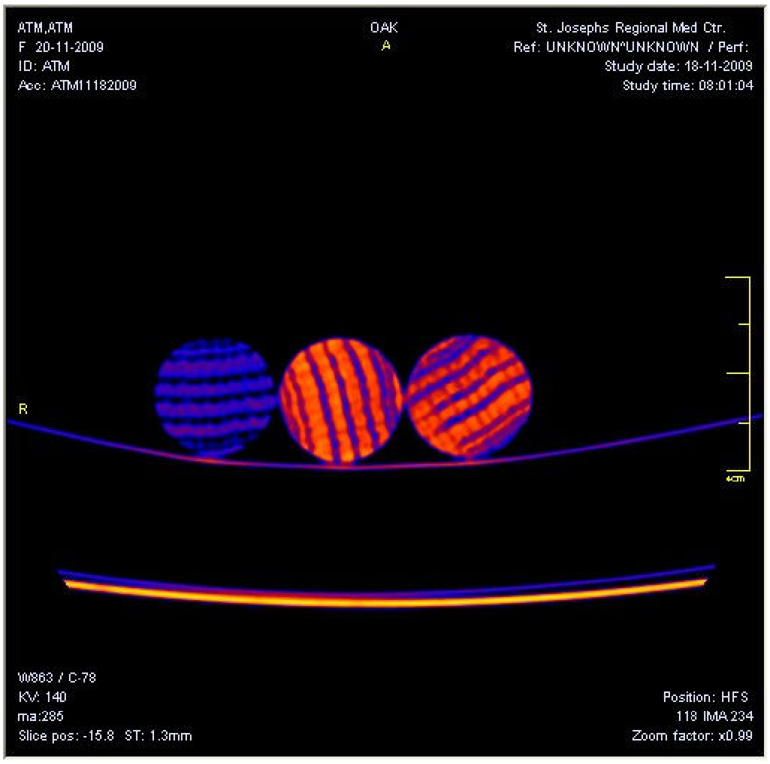

Figure 32 – CT scan of the impregnation process in White Oak Dowel (KV:140; ma: 285; Slice: -15.8; original zoom factor: 0.99).

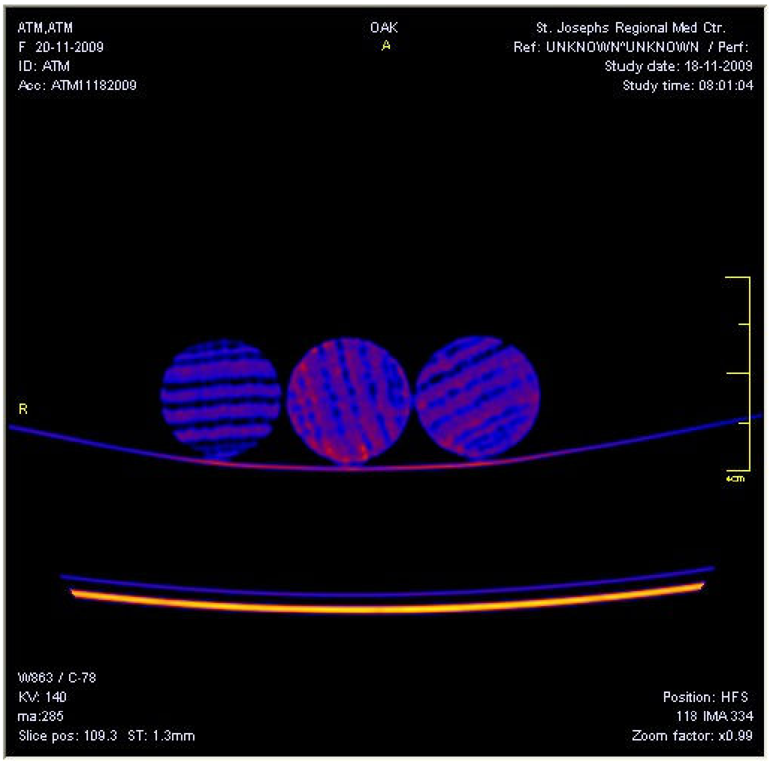

Figure 33 – CT scan of the impregnation process in White Oak Dowel (KV:140; ma: 285; Slice: 109.3; original zoom factor: 0.99).

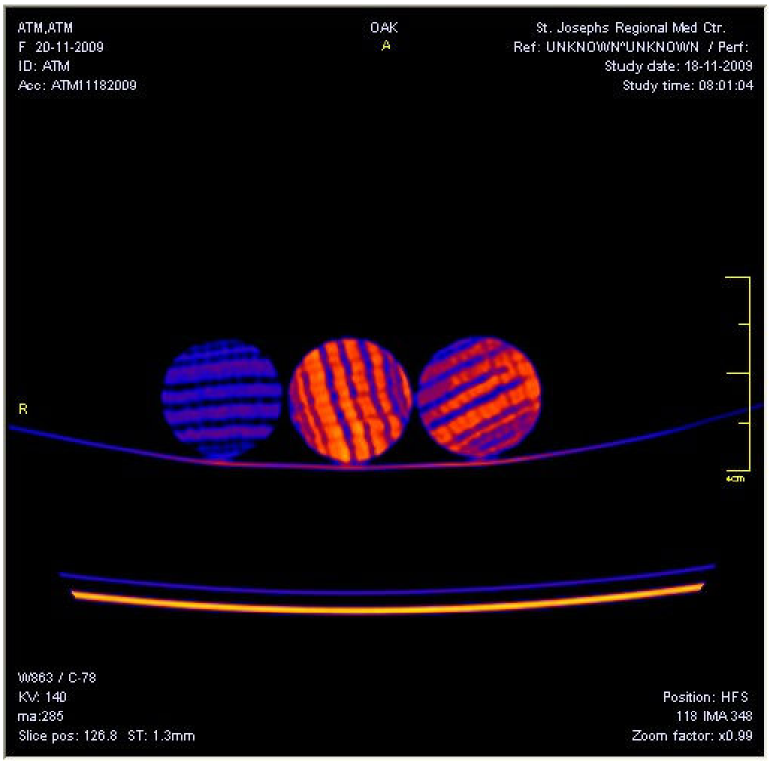

Figure 34 – CT scan of the impregnation process in White Oak Dowel (KV:140; ma: 285; Slice: 126.8; original zoom factor: 0.99).

22.2.3.3. *Ulmus spp.*, Elm from China

22.2.3.3.1. Macroanalysis

The Q1-3563 and SDF-5 impregnated dowels of the Elm presented a brownish yellow color (10YR 6/6 by Munsell reference colors) different from the natural Control color (Fig. 35).

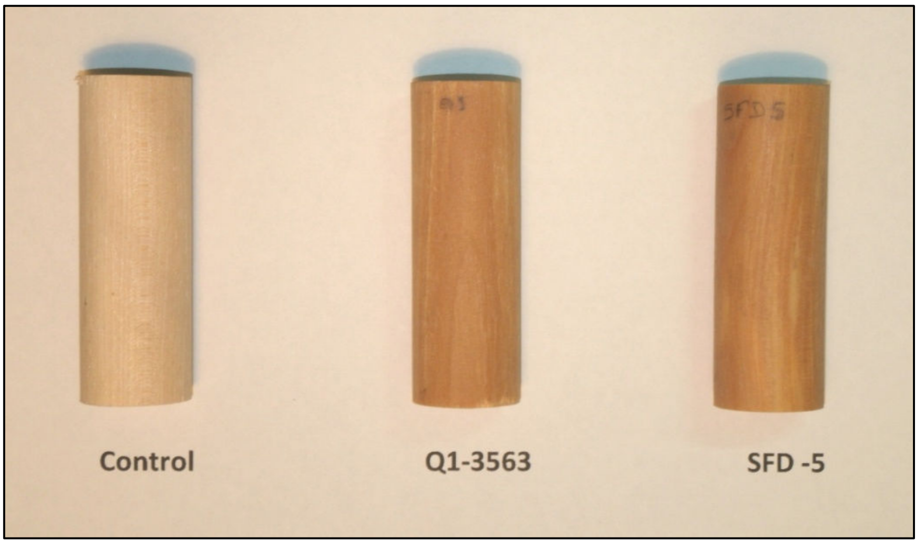

Figure 35 – Aspect of the Elm Dowel with Control, Q1-3563 and SFD-5 treatment.

A significant increase in the mass parameter (Table 7) was observed with Q1-3563 treatment (26.2%) and with SFD-5 (21.3%). This is another wood from the hardwood group and in this case with a mass density of 820 Kgm^{-3}. This value of mass density represents higher levels of fibers and micro pores in the tissues and in that way makes it more able to conserve silicone oil in the interior of the cells.

Analyzing the length of the Elm dowels, it is possible to verify that Q1-3563 treatment increased this factor in 1.5% and 1.2% for the SFD-5 treatment. Once more differences between them are not significant.

In the width/diameter factor, the change of these values is confirmed with the Q1-3563 treatment increasing in 2.3% and 1.2% increasing for the sample SFD-5.

Table 7 – Data of the Elm Dowel before and after application of the silicone oil.

	Elm (dowel cylinder)								
	Mass (g)			Length (cm)			Width/Diameter (cm)		
Treatment	Before	After	Change (%)	Before	After	Change (%)	Before	After	Change (%)
Control	25.90	25.90	0.00	7.33	7.33	0.00	2.40	2.40	0.00
Q1-3563	25.38	34.40	26.20	7.23	7.34	1.50	2.40	2.47	2.80
SFD-5	25.90	32.90	21.30	7.28	7.37	1.20	2.40	2.46	2.40

22.2.3.3.2. Microanalysis

The CT scan images of the Elm, demonstrate that samples treated with Q1-3563 pass more through the cell tissue than with SFD-5 treatment (Fig. 36-38). In this sequence of images, the red color represents the tissues with silicone oil (Q1-3563 and SFD-5), the red-blue color indicates less quantity of the silicone oil in the tissue.

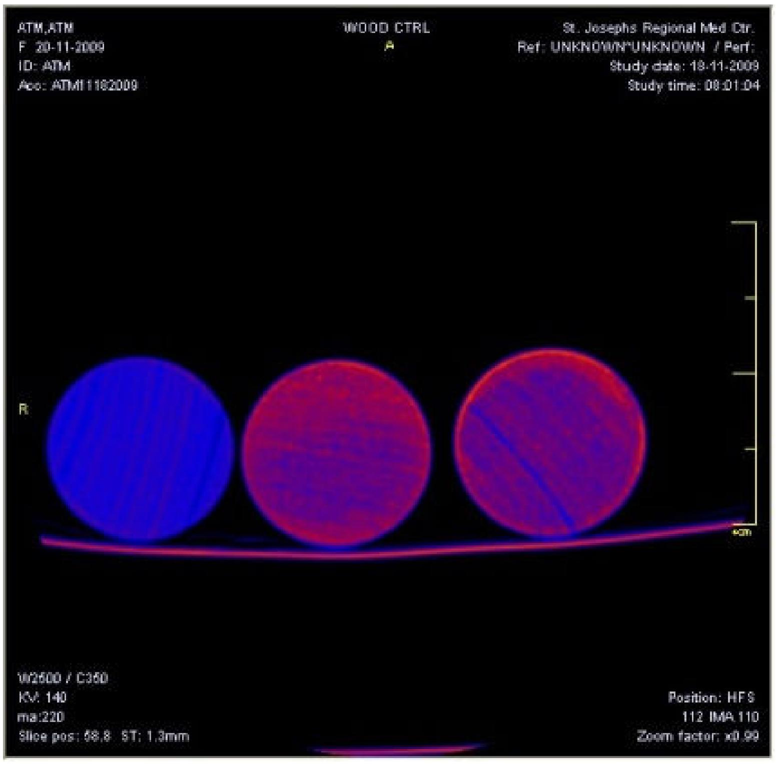

Figure 36 – CT scan of the impregnation process in Elm Dowel (KV:140; ma: 220; Slice 38.8; original zoom factor: 0.99).

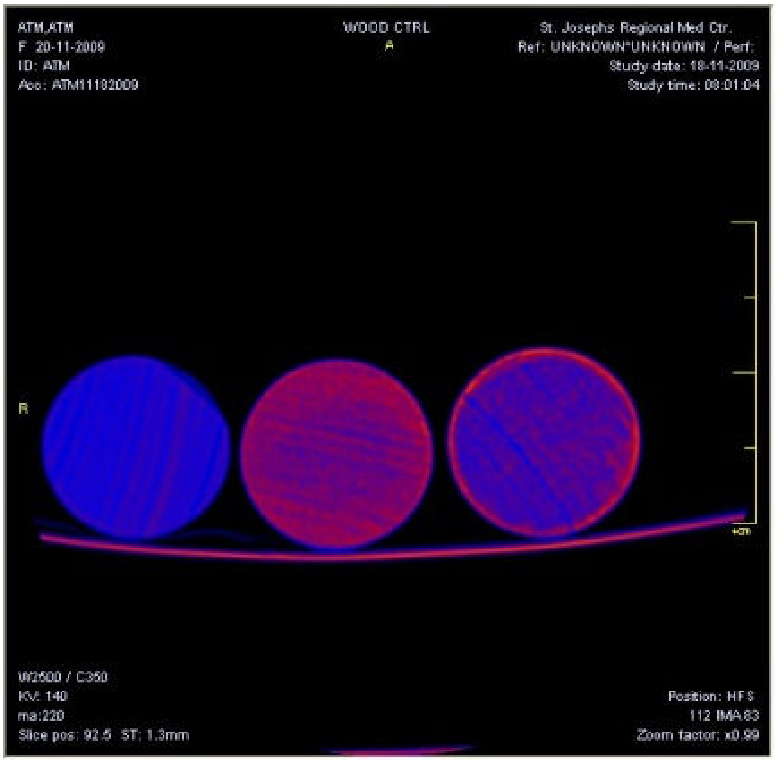

Figure 37 – CT scan of the impregnation process in Elm Dowel (KV:140; ma: 220; Slice 92.5; original zoom factor: 0.99).

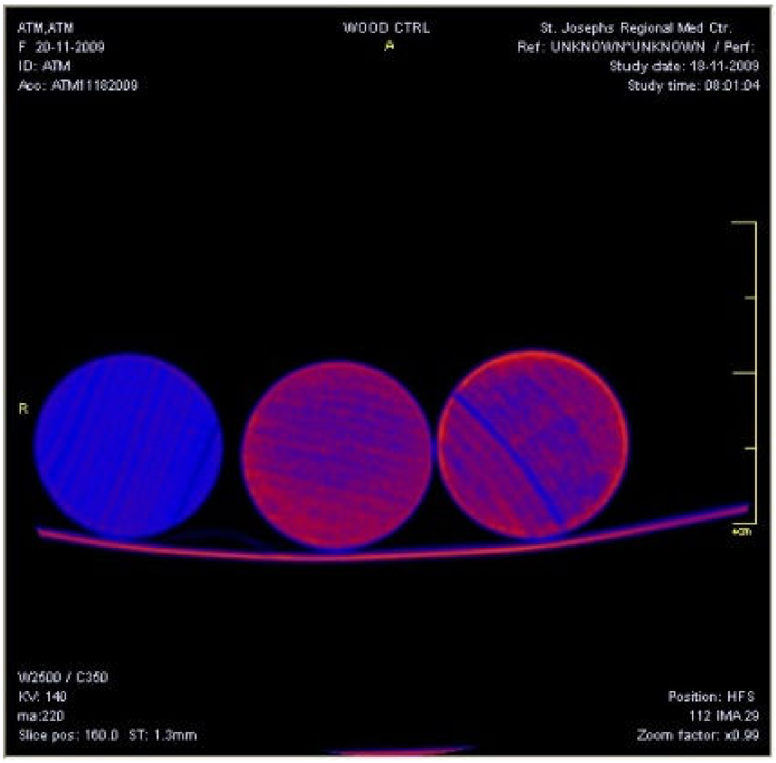

Figure 38 – CT scan of the impregnation process in Elm Dowel (KV:140; ma: 220; Slice 160.0; original zoom factor: 0.99).

22.2.4. Discussion

Silicone oils are used to give some structural capacity to waterlogged archaeological woods. In this case two silicone oils Q1-3563 and SFD-5 were used in different types of woods. It was proved that the Q1-3563 treatment has the higher capacity to saturate the woods rather than SFD-5. The main reason is because it has the minor viscosity (72cst) which helps it to easily pass through the different wood mass densities[448].

The impregnation with silicone oils increases the mass, length and width parameters, a situation that must be considered in each treatment. Nevertheless, this feature is not that visible when Q1-3563 treatment is applied to hardwoods.

Considering these changes, with this experiment, it is possible to say that hardly ever when an impregnation treatment is performed artifacts go back to their original form.

22.3. Silicone oil removal, the *La Belle* treenails experiment

22.3.1. Objectives and research plans

The main purpose of preserving archaeological remains is to safeguard them to obtain scientific information about human culture. Conservation, with all its scientific techniques, is the key to maintaining and preventing artifacts degradation. An important part of conservation, besides sustaining the integrity of its aesthetic values and structure features, is the reversibility of the preservation process. For many authors this is seen as an impossible principle; others describe it as theoretical ideal; while others have already proved that no treatment is reversed at a molecular level[449].

The cross-linking polymers, used for archaeological conservation, are irreversible. This is due to their ability to establish covalent bond with materials and also their high stability. Nevertheless, their use in some particular cases is recognized as a necessity.

Being aware of the chemical characteristics of silicone, but also considering the need to perform experiments in the extraction of it, two treenails conserved 10 years ago

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[448] LUDWICK, Lena - A comparative study of surface treatments... p14.

[449] HORIE, C. V. – *Op. cit.*

with silicone oils were selected to perform the removal of silicone oils used in its treatment.

For this purpose, two chemical products; potassium nitrate (KNO_3) and 3M^{TM} Cleaner (Cleaner) were used and the consequent reaction analyzed.

In the past, potassium was used to cause a reduction of potassium fluorosilicate ($4\ K + K_2SiF_6 \rightarrow Si + 6\ KF$) to produce silicate[450].

Nowadays, silicone oils present a more complex chemical structure. Nevertheless, following the potassium fluorosilicate reduction process and the unpublished work, and under the guidance of Dr. Wayne Smith in this area of knowledge, in this experiment we used potassium nitrate (KNO_3) as a source of potassium in order to promote the reduction and removal of silicone.

To compare the action of the nitrate potassium in the silicone oils, we used a commercial product named Citrus Base Cleaner from 3M^{TM}, composed of volatile organic compounds, such as ketones, carbon monoxide, carbon dioxide, aldehydes and hydrocarbons which are widely used in industry to safely remove a wide range of glues, adhesives and polymers.

This experiment intended to understand if it was really feasible to perform and if during the removal there was any destruction of the archaeological objects or their chemical structure.

22.3.2. Materials and methods

Two treenails from *La Belle*[451], a seventeenth-century shipwreck, were chosen for the removal of their silicone content. They had already been submitted to a desalination process and stabilization through silicone oil[452], a treatment that was performed by the team of the APRL, TAMU, 10 years ago. The process of conservation of the treenails consisted in the desalination for 24 months in freshwater baths, followed by the extraction of water. The extraction of water was accomplished by a series of three ethanol baths, followed by three acetone dehydration baths, each baths lasting one

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[450] Dow Corning - Silicone Chemistry Overview… p. 2.

[451] BRUSETH, J; TURNER, T. – *Op. cit.*

[452] SMITH, C. Wayne a) – *Op. cit.* p. 45-50.

week[453]. For the stabilization, the standard procedure of APRL was carried out. Thus, the treenails were impregnated with a solution of CR-20 (viscosity of 1.00 cSt), a cross-linker MTMS and placed in a vacuum chamber, where the pressure was gradually decreased. After applying vacuum, the pressure was gradually re-established and the treenails drained and the excess of the mixture was wiped off. The last step of silicone treatment was to expose the treenails to a 15 g of catalyst DBTDA for 24 hours.

The two treenails were cut (Fig. 39-41) and divided into two groups, Group 1 and Group 2, with a total of nine samples in each:

Group 1 - was composed of three samples with no treatments named Control plus two samples treated with potassium nitrate (KNO_3) and two samples with a treatment of a 3M™ Cleaner (Cleaner).

Group 2 - was composed of three samples with no treatment, identified as Control; three samples treated with KNO_3; and three samples with a treatment of Cleaner.

Figure 39 – Aspect of the treenails before treatments.

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[453] *Idem*, p. 50.

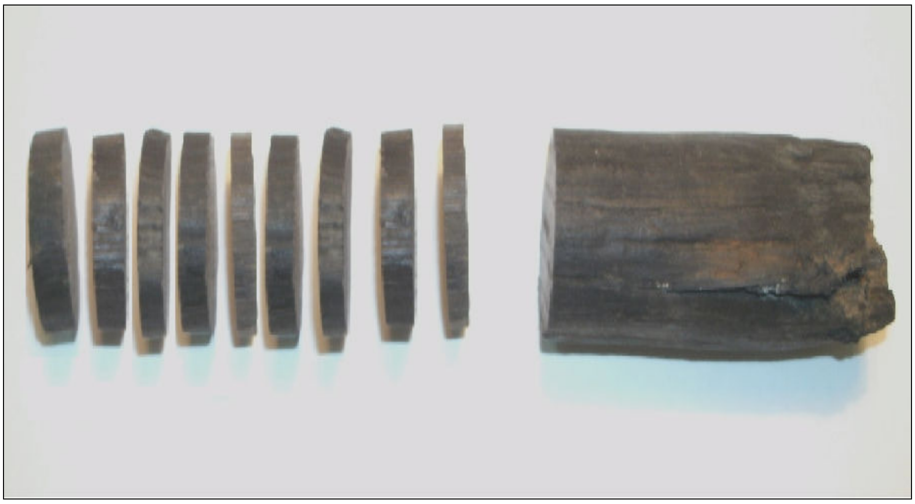

Figure 40 – Aspect of Treenail 1 after being cut.

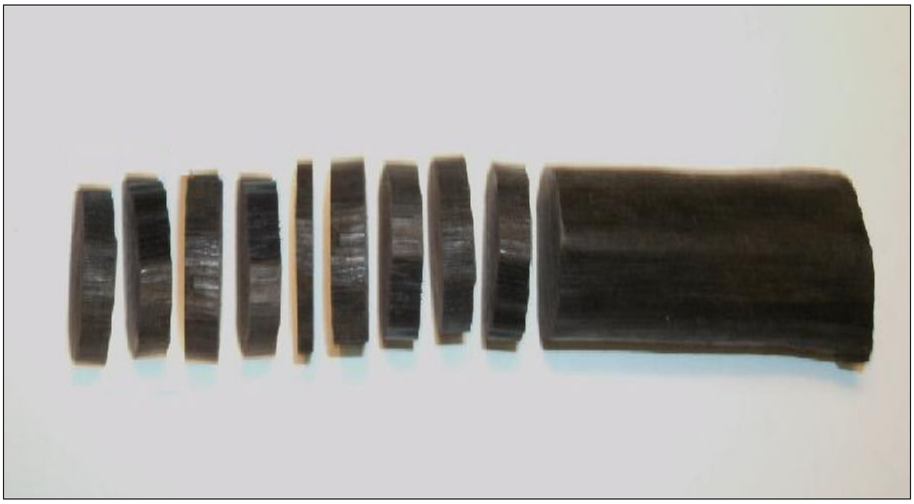

Figure 41 – Aspect of Treenail 2 after being cut.

Samples labeled Potassium Nitrate were introduced into a beaker with a solution composed of 15g of potassium nitrate, 250 ml of ethanol and 250 ml of DI water. This solution was changed by a fresh one every three days for two weeks.

Samples labeled Cleaner were submerged, into a beaker, directly in a commercial product named Citrus Base Cleaner from 3M^{TM}. This solution was changed every three days for two weeks.

When the samples were put in the beakers, they were sealed and kept at ambient pressure and room temperature. Before putting the samples in a fresh solution, all of them were examined with a microscope, searching for any micro-morphological alterations.

To remove the excess of the residuum of the Potassium Nitrate and the Cleaner, ethanol was used; after which samples were placed on absorbent paper.

Four samples (1 Control, 1 Potassium Nitrate and 2 Cleaner) were transferred to the Microscopic and Imaging Center (MIC) at TAMU, to identify the state of the cell wall by a Scanning Electron Microscope (SEM) and to determine by Electron Dispersion Spectroscopy (EDS) the levels of the main elements present in the samples.

22.3.3. Scanning electron microscopy (SEM / EDS)

The Scanning electron microscopy (SEM) is equipped with energy dispersive x-ray fluorescence detection (EDS). The JEOL JSM-6400 software-oriented, analytical-grade SEM was the equipment used to acquire all digitized images. JSM-6400 was equipped with a PGT EDS System, which makes it capable of distinguishing different elements, showing the level or the intensity of the chemical elements present in the different wood sample.

The analyses were carried out at the Microscopy and Imaging Center (MIC) at TAMU, by Ann Ellis and Dr. Michael Pendleton, who also took the responsibility of preparing the samples. The samples were delivered completely dry, and a thin graphite layer was applied. After coating each surface, samples were mounted on a sample holder with sulfur free glue.

22.3.4. Statistical method

Mean, variance, and coefficient of variation (cv) were computed for each treenail treatment. A normality test was performed to verify the hypothesis, assuming each property has a normal variable distribution in the variables, and these variables without a normal distribution subjected to a log-transformation.

After verifying the normality of sample distribution and homogeneity of variances, mean average parameters studied (mass, length and thickness of the treenails) were compared using one-way analysis of variance (ANOVA), followed by multiple comparison Duncan's post-test. Linear correlations among treenails properties were also determined. Differences were considered significant when $p<0.05$. Normality of sample distribution and homogeneity of variances were verified before ANOVA[454].

For a better understanding, the information is presented in two categories: first a macro analysis where we analyzed the percentage differences that resulted between changes in values before and after the experiment for the mass, length and thickness content in the treenail 1 and 2, through the analysis of variance (ANOVA), and the means compared using the Duncan Multiple Range Test (DMRT) at the 95% significance level, using the SPSS 11.0 software program for statistical analysis.

In the Duncan test, the columns obtained from the figures represent different treatments on each treenail and treatments with the same letter were not significantly different at $P<0.05$ (Duncan Test). For example, a treatment with the statistical result which presents the letter a, is significantly different from a treatment with the letter b.

Microanalysis is the second group and presents the information obtained from SEM micrograph and EDS spectrum samples for each treatment (Control, Potassium Nitrate and Cleaner).

22.3.5. Results and discussion

The data obtained by the Macro and Microanalysis are presented according to each treenail.

22.3.5.1. Macroanalysis

22.3.5.1.1. Treenail 1

22.3.5.1.1.1. Mass

Analyzing the mass content in the different treatments of the samples obtained from treenail 1 (Table 8), we verify a loss of the mass content in the samples treated with KNO_3 and Cleaner compared to the Control samples. The reduction of the mass content in the KNO_3 treatment was 3.66% and 18.75% for the Cleaner treatment (Fig. 42).

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[454] ZAR, J.H. - Biostatistical Analysis...

Through ANOVA analyses and statistically analyzing the Duncan Test results (see Appendix I), both show that the values of the contents in mass of the Control, KNO_3 and Cleaner treatments are completely and significantly different between them (letters a, b and c).

22.3.5.1.1.2. Length

For the Length parameter, we identified a shrinkage phenomena in the samples treated with the KNO_3 and Cleaner compared to Control (Table 8). The Cleaner samples presented -2.46% and -0.67% for the KNO_3 thus the bigger average of shrinkage belongs to the Cleaner (Figure 43).

Using the Duncan test and ANOVA data for this parameter, massive and significant differences (letters a, b and c) between the treatments are also verified (see Appendix I).

22.3.5.1.1.3. Thickness

In the Thickness factor, the same issue of shrinkage was found as verified in the Length parameter. The samples of the Cleaner treatment presented an average of -11.48% (Table 8) and -2.89% for the KNO_3 (Figure 44).

Analyzing the data by the Duncan test, we verified enormous differences (letters a, b and c) between treatments and higher significance through ANOVA results (see Appendix I).

Table 8 – Data of Treenail 1 before and after application of the different treatments.

Treatments	**Mass**			**Length**			**Thickness**		
	Before (g)	**After (g)**	**Change (%)**	**Before (cm)**	**After (cm)**	**Change (%)**	**Before (cm)**	**After (cm)**	**Change (%)**
Control	2.70	2.70	0.00	2.52	2.52	0.00	0.56	0.56	0.00
	2.60	2.60	0.00	2.59	2.59	0.00	0.54	0.54	0.00
	2.50	2.50	0.00	2.52	2.52	0.00	0.57	0.57	0.00
Average			**0.00**			**0.00**			**0.00**
KNO_3	2.50	2.40	- 4.00	2.54	2.53	- 0.39	0.56	0.54	- 3.57
	2.60	2.50	- 3.85	2.65	2.63	- 0.75	0.52	0.51	- 1.92
	2.55	2.47	- 3.14	3.50	3.47	- 0.86	0.63	0.61	- 3.17
Average			**- 3.66**			**- 0.67**			**- 2.89**
Cleaner	2.60	2.10	- 19.23	2.67	2.60	- 2.62	0.49	0.43	- 12.,24
	2.70	2.20	- 18.52	2.53	2.47	- 2.37	0.61	0.54	- 11.48
	2.65	2.16	- 18.49	2.50	2.44	- 2.40	0.56	0.50	- 10.71
Average			**- 18.75**			**- 2.46**			**- 11.48**

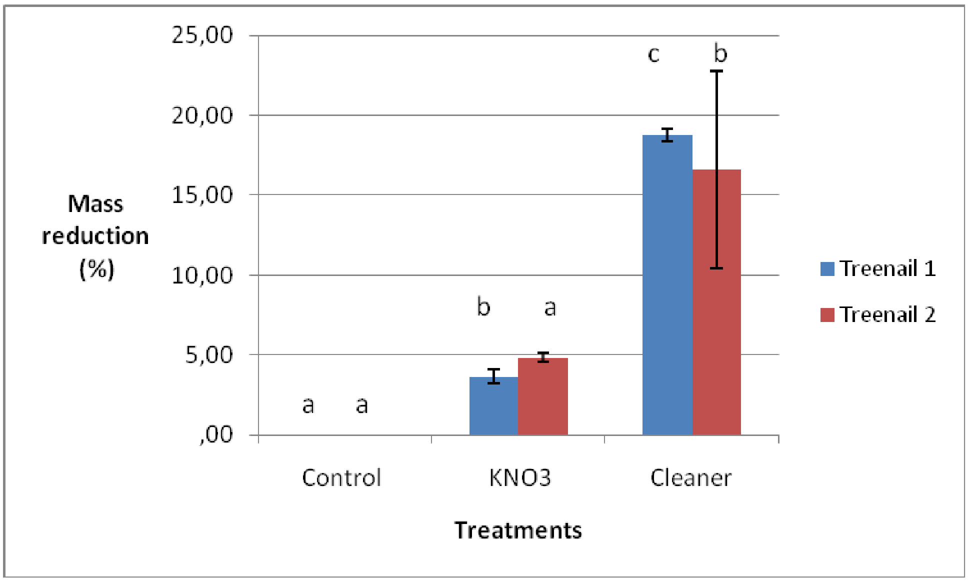


Figure 42. Evolution of the Mass content in Treenail 1 and 2. Values for the different treatments: Control, KNO3 and Cleaner. Columns for each treenail with the same letter were not significantly different at P<0.05 (Duncan Test).

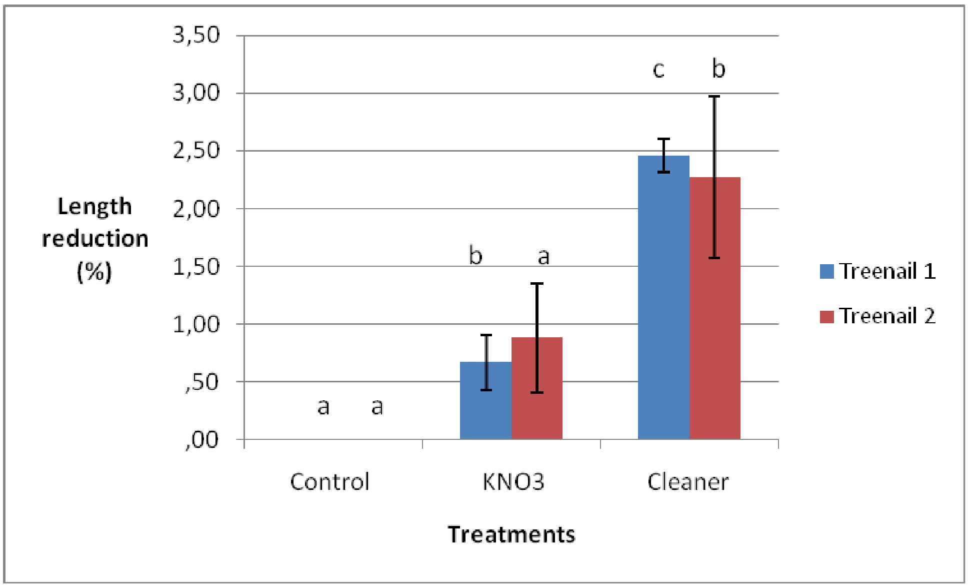


Figure 43. Evolution of the Length content in Treenail 1 and 2. Values for the different treatments: Control, KNO3 and Cleaner. Columns for each treenail with the same letter were not significantly different at P<0.05 (Duncan Test).

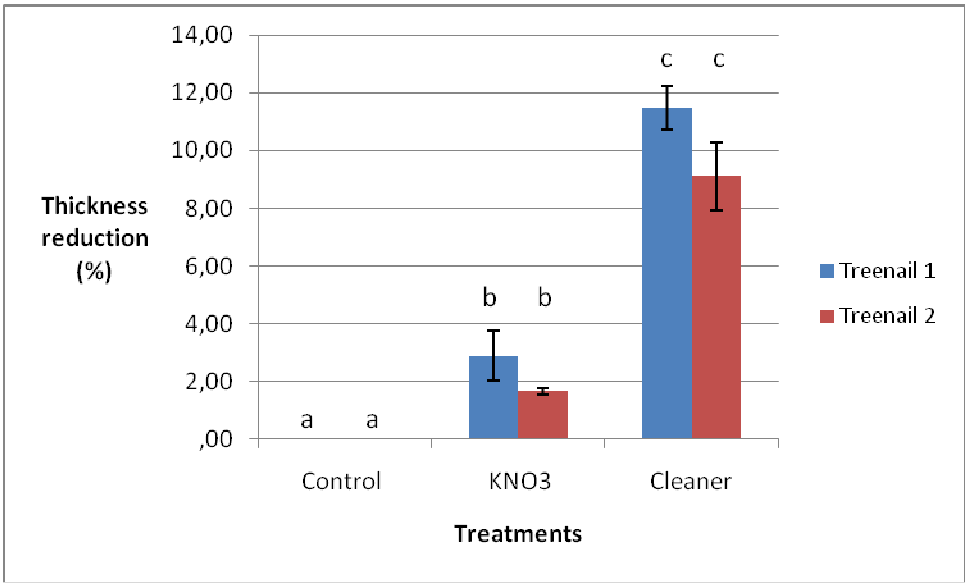


Figure 44. Evolution of the Thickness content in Treenail 1 and 2. Values for the different treatments: Control, KNO3 and Cleaner. Columns for each treenail with the same letter were not significantly different at P<0.05 (Duncan Test).

22.3.5.1.2. Treenail 2

22.3.5.1.2.1. Mass

Observing the Mass content in the different samples of Treenail 2, we verified weight lost in the samples treated with KNO_3 and Cleaner. Compared to Control, the Cleaner samples presented a higher average of mass losing, -16.62%, and the KNO_3 samples - 4.85% (Table 9 and Figure 42).

With the Duncan test small differences between KNO_3 and Control treatments (letter a) were verified, however, these two are totally different to the Cleaner treatment (letter b). The ANOVA analysis indicates significant differences between them (see Appendix II).

22.3.5.1.2.2. Length

For the Length parameter on this treenail, shrinkage phenomena in the samples treated with the KNO_3 and Cleaner were observed.

Analyzing the data through the Duncan test and ANOVA (see Appendix II), major contraction was verified with - 2.27% in the samples treated with the Cleaner, and - 0.88% for the samples treated with the KNO_3 (Table 9), when compared with Control samples (Figure 43). Statistically, the Control and KNO_3 treatments present small differences between them (letter a), but are completely different from the Cleaner treatment (letter b).

22.3.5.1.2.3. Thickness

A reduction of the Thickness parameter was verified in the treated samples. When compared to control, Cleaner samples statistically presented an average of a decrease of -9.12% and KNO_3 in about -1.66% (Table 9) (Figure 44). The Duncan test shows that the values of the treatments Control, Cleaner and KNO_3 are completely different (letters a, b and c) and ANOVA presents significantly higher differences between them (see Appendix II).

Table 9 – Data of Treenail 2 before and after application of the different treatments.

Treatments	**Mass**			**Length**			**Thickness**		
	Before (g)	**After (g)**	**Change (%)**	**Before (cm)**	**After (cm)**	**Change (%)**	**Before (cm)**	**After (cm)**	**Change (%)**
Control	2.30	2.30	0.00	2.36	2.36	0.00	0.68	0.68	0.00
	2.10	2.10	0.00	2.47	2.47	0.00	0.60	0.60	0.00
	1.80	1.80	0.00	2.27	2.27	0.00	0.53	0.53	0.00
Average			**0.00**			**0.00**			**0.00**
KNO_3	2.00	1.90	- 5.00	2.29	2.27	- 0.87	0.56	0.55	- 1.79
	2.20	2.10	- 4.55	2.38	2.37	- 0.42	0.61	0.60	- 1.64
	2.00	1.90	- 5.00	2.21	2.18	- 1.36	0.65	064	- 1.54
Average			**- 4.85**			**- 0.88**			**- 1.66**
Cleaner	2.00	1.80	- 10.00	2.41	2.37	- 1.66	0.57	0.52	- 8.77
	1.70	1.40	- 17.65	2.31	2.24	- 3.03	0.48	0.43	- 10.42
	1.80	1.40	- 22.22	2.37	2.32	- 2.11	0.49	0.45	- 8.16
Average			**- 16.62**			**- 2.27**			**- 9.12**

22.3.5.2.Microanalysis

The microanalysis presented corresponds to the SEM micrograph and EDS spectrum for Control, KNO_3 and 3M^{TM} Cleaner (Cleaner) samples. In the Control sample three distinct areas were analyzed. In the sample treated with KNO_3 two areas were examined. Finally, in the Cleaner samples five different areas were studied, two in sample one and three for the second sample.

22.3.5.2.1. Control

In the Control sample, not subject to any removal of silicone, the SEM micrograph presents images with a collapsed cell wall, with plenty of white dots (Figure 45-47) which represents areas with high levels of lead (Pb), silicon (Si), and iron (Fe) As for the EDS spectrum, the three random spots of the control sample indicate the high presence of iron (Fe), lead (Pb) and silicon (Si), elements measured in KeV (Figure 48-50). This could probably be caused by contamination of the Si with Pb and Fe during the process of the consolidation treatment.

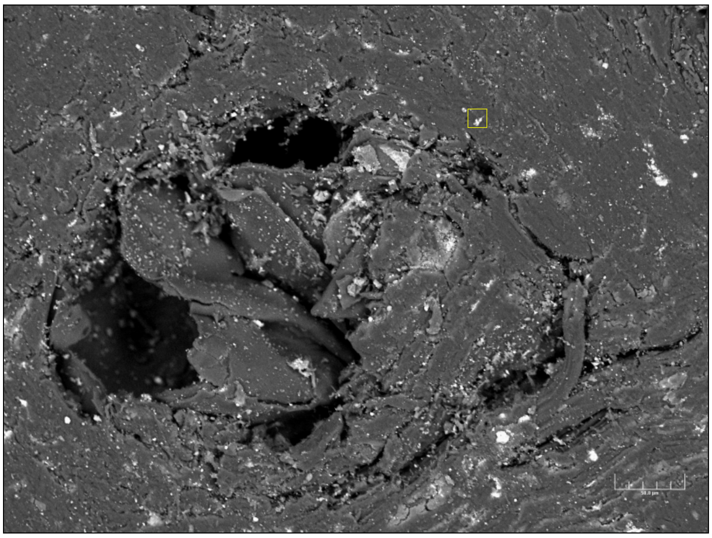


Figure 45. SEM micrograph in spot 1 of the Control sample (original zoom factor: 250x and 15Kv).

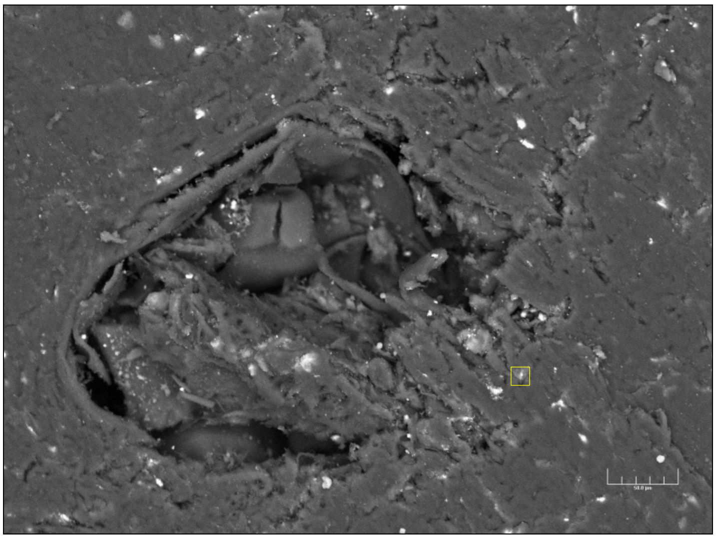


Figure 46. SEM micrograph in spot 2 of the Control sample (original zoom factor: 250x and 15Kv).

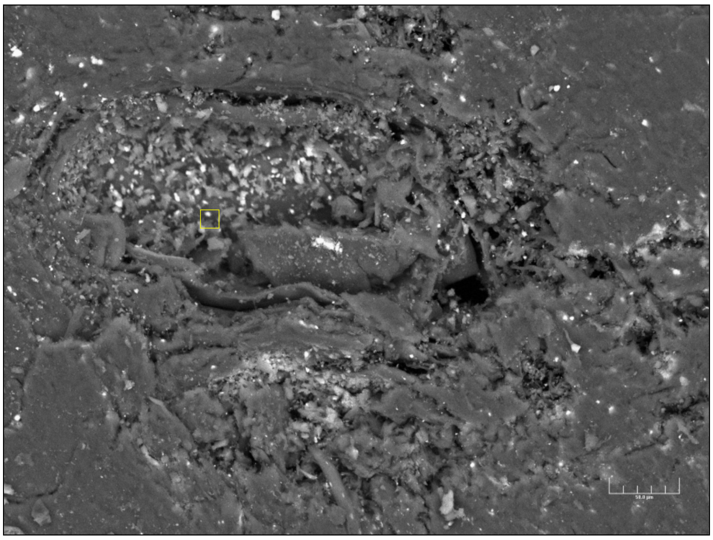
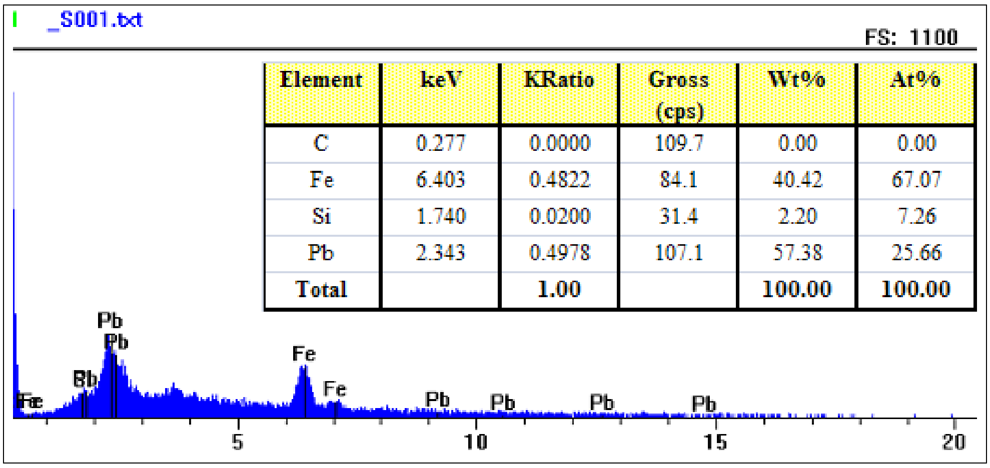
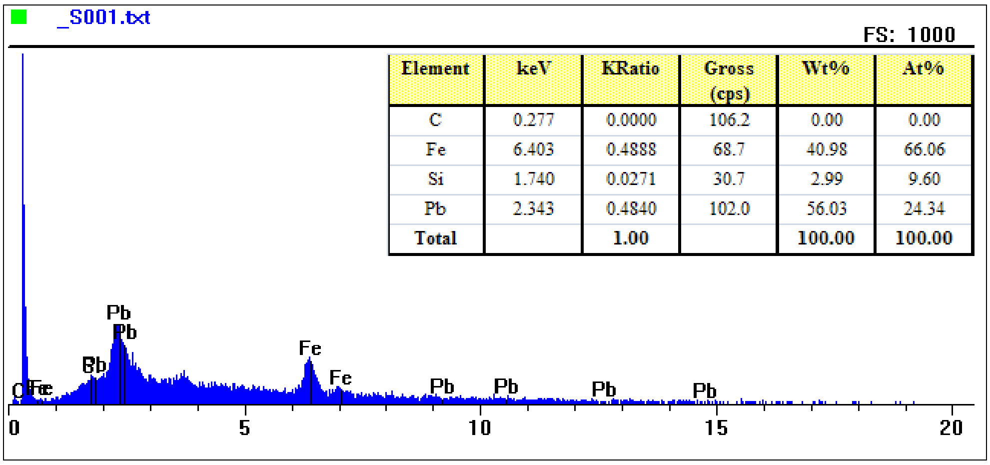


Figure 47. SEM micrograph in spot 3 of the Control sample (original zoom factor: 250x and 15Kv).



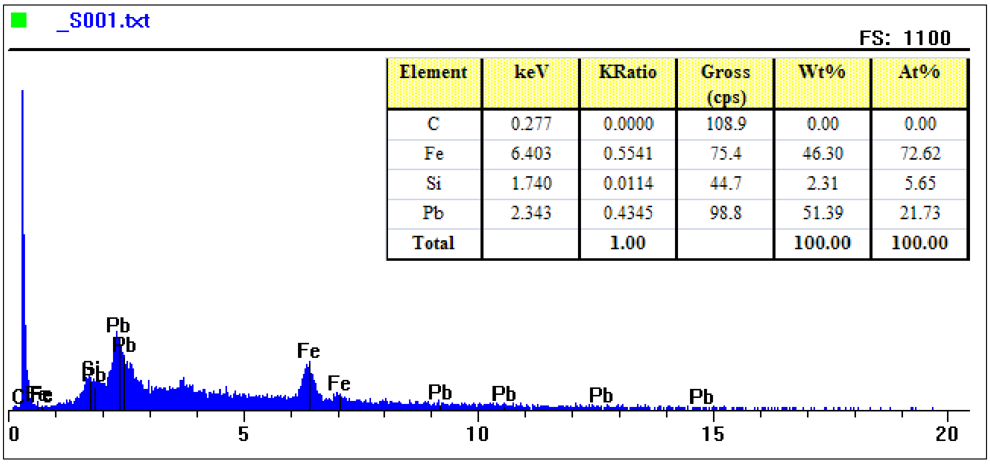
Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	109.7	0.00	0.00
Fe	6.403	0.4822	84.1	40.42	67.07
Si	1.740	0.0200	31.4	2.20	7.26
Pb	2.343	0.4978	107.1	57.38	25.66
Total		1.00		100.00	100.00

Figure 48. EDS spectrum of spot 1 of the Control sample (measured in Kev).



Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	106.2	0.00	0.00
Fe	6.403	0.4888	68.7	40.98	66.06
Si	1.740	0.0271	30.7	2.99	9.60
Pb	2.343	0.4840	102.0	56.03	24.34
Total		1.00		100.00	100.00

Figure 49. EDS spectrum of spot 2 of the Control sample (measured in Kev).



Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	108.9	0.00	0.00
Fe	6.403	0.5541	75.4	46.30	72.62
Si	1.740	0.0114	44.7	2.31	5.65
Pb	2.343	0.4345	98.8	51.39	21.73
Total		1.00		100.00	100.00

Figure 50. EDS spectrum spot 3 of the Control sample (measured in Kev).

22.3.5.2.2. Potassium nitrate

For the sample treated with KNO_3 for the removal of silicone oil (Figure 51-52), the SEM micrograph also presented images with collapsed cells wall but with fewer white dots, compared to the control treatment.

The EDS spectrum in the two random spots of the sample (Figure 53-55) indicated a high presence of Potassium (K), iron (Fe) and silicon (Si), elements measured in KeV.

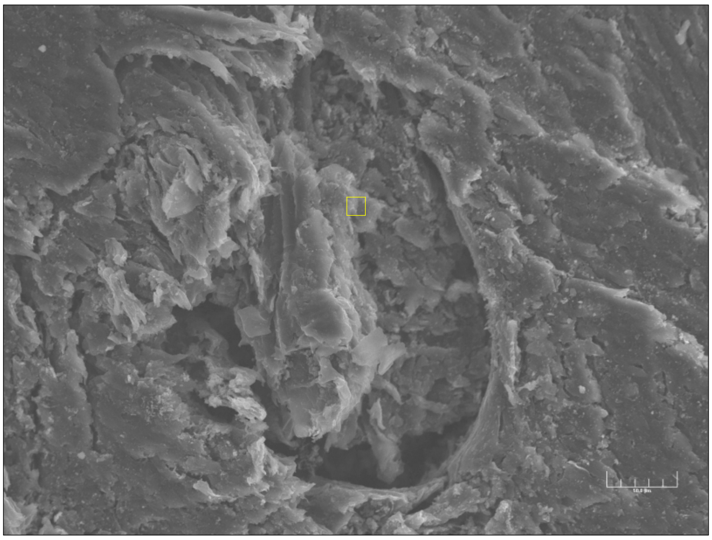


Figure 51. SEM micrograph in spot 1of the KNO_3 sample (original zoom factor: 250x and 15Kv).

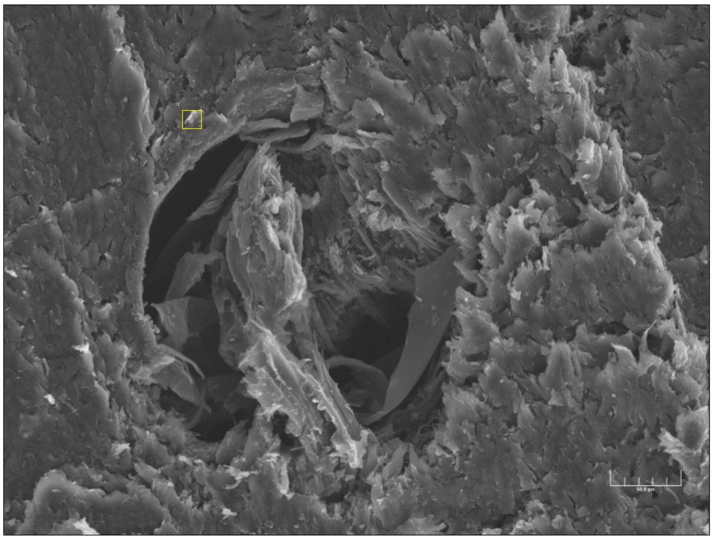
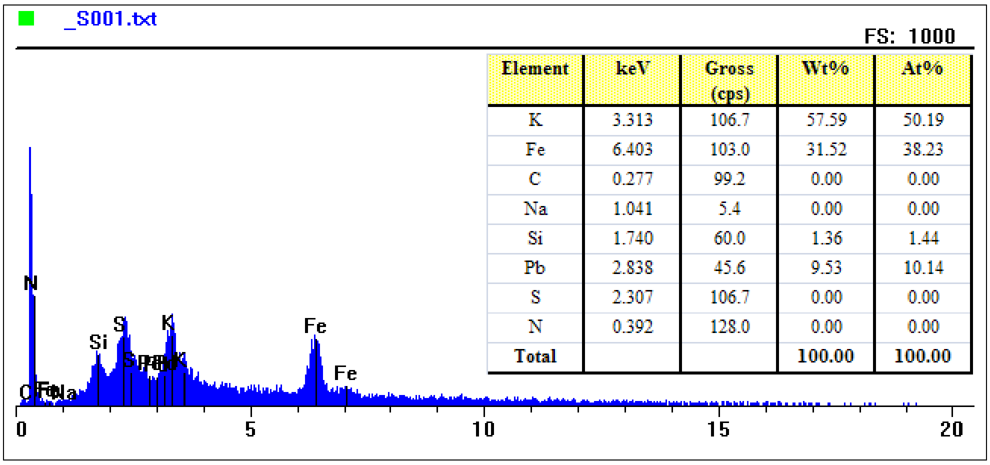
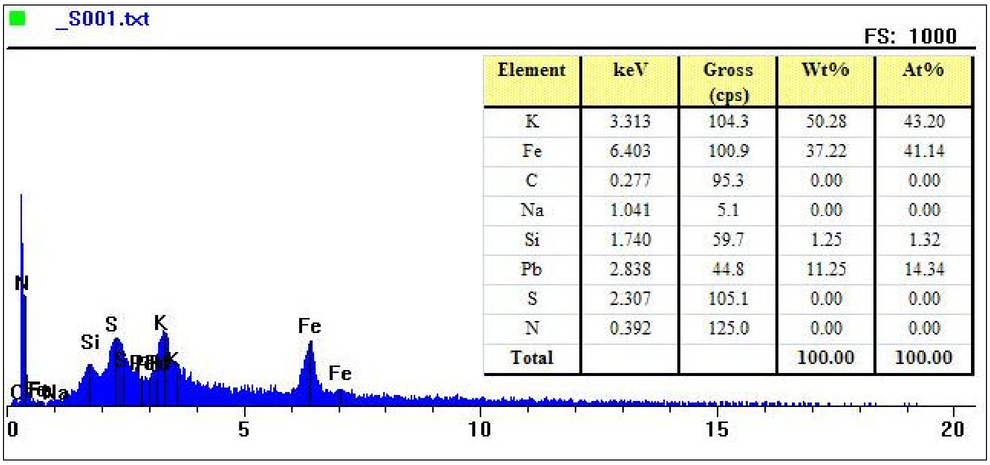


Figure 52. SEM micrograph in spot 2 of the KNO_3 sample (original zoom factor: 250x and 15Kv).



Element	keV	Gross (cps)	Wt%	At%
K	3.313	106.7	57.59	50.19
Fe	6.403	103.0	31.52	38.23
C	0.277	99.2	0.00	0.00
Na	1.041	5.4	0.00	0.00
Si	1.740	60.0	1.36	1.44
Pb	2.838	45.6	9.53	10.14
S	2.307	106.7	0.00	0.00
N	0.392	128.0	0.00	0.00
Total			100.00	100.00

Figure 53. EDS spectrum of spot 1of the KNO_3 (measured in Kev).



Element	keV	Gross (cps)	Wt%	At%
K	3.313	104.3	50.28	43.20
Fe	6.403	100.9	37.22	41.14
C	0.277	95.3	0.00	0.00
Na	1.041	5.1	0.00	0.00
Si	1.740	59.7	1.25	1.32
Pb	2.838	44.8	11.25	14.34
S	2.307	105.1	0.00	0.00
N	0.392	125.0	0.00	0.00
Total			100.00	100.00

Figure 54. EDS spectrum of spot 2 of the KNO_3 sample (measured in Kev)

22.3.5.2.3. Cleaner

The SEM micrograph for the samples treated with Cleaner, from 3M^{TM}(Figure 55-59), showed that the cell wall structure was also collapsed, however, with just few white dots, almost presenting a clean tissue compared with the Control and the Potassium Nitrate treatment.

The EDS spectrum was applied in two random spots for sample one and three random spots in sample two (Figure 60-64), all of them indicating a high presence of iron (Fe), lead (Pb), sulfur (S), and a residual presence of silica (Si), all the elements measured in KeV.

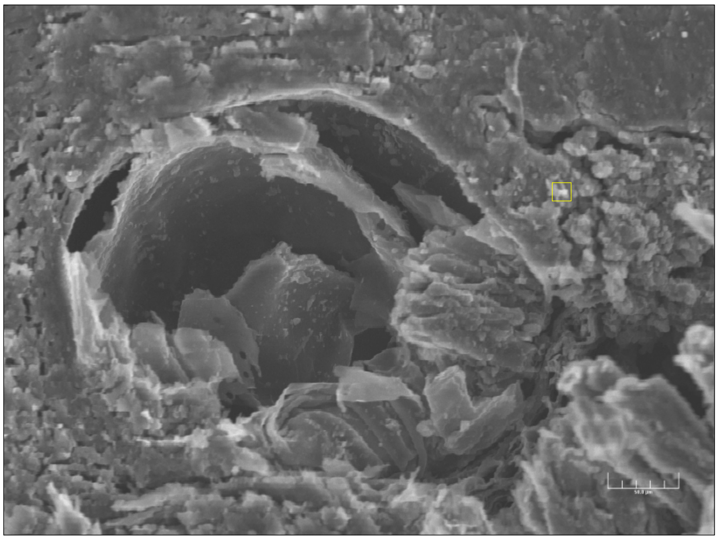


Figure 55. SEM micrograph of the Cleaner sample 1 area 1 (original zoom factor: 250x and 15Kv).

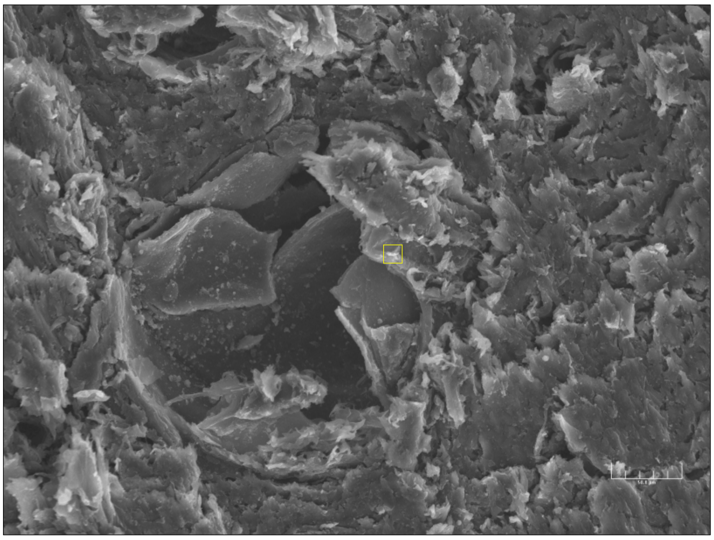


Figure 56. SEM micrograph of the Cleaner sample 1 area 2 (original zoom factor: 250x and 15Kv).

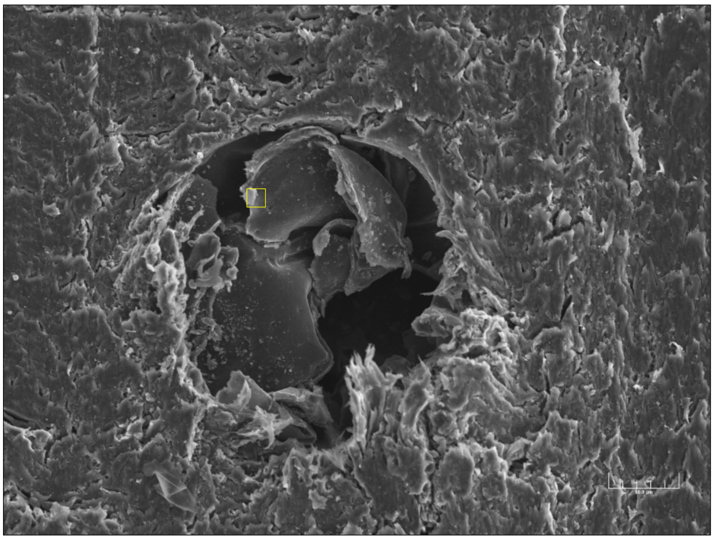


Figure 57. SEM micrograph of the Cleaner sample 2 area 1 (original zoom factor: 250x and 15Kv).

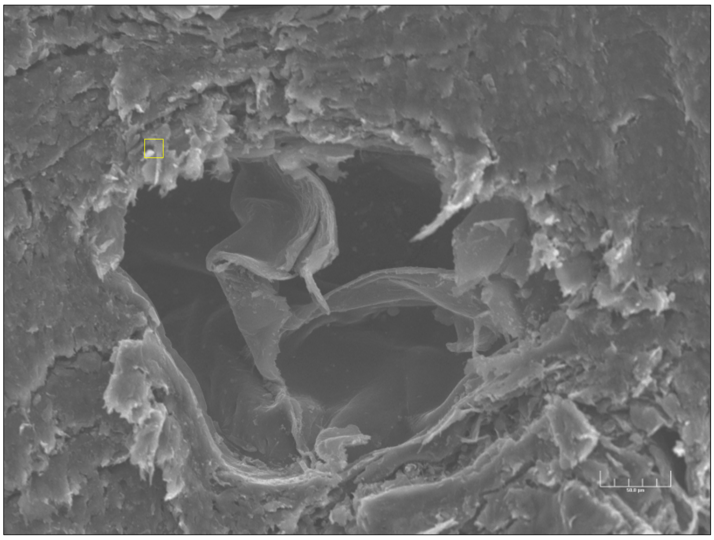


Figure 58. SEM micrograph of the Cleaner sample 2 area 2 (original zoom factor: 250x and 15Kv).

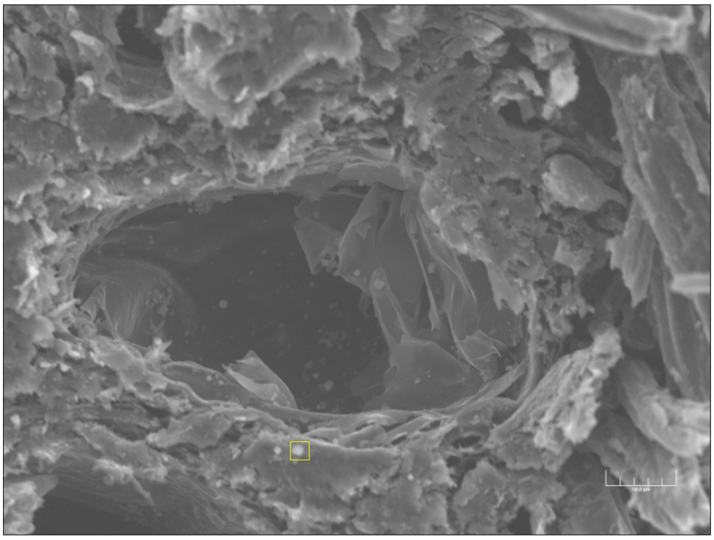
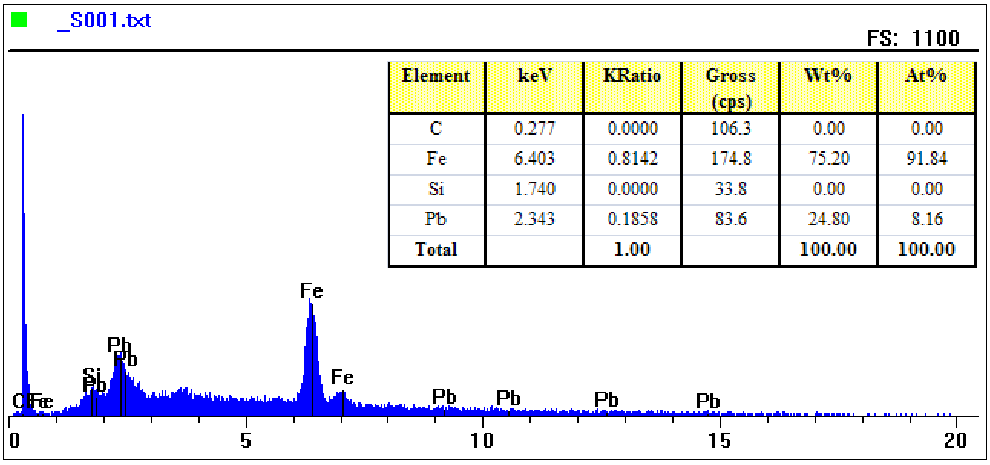


Figure 59. SEM micrograph of the Cleaner sample 2 area 3 (original zoom factor: 250x and 15Kv).



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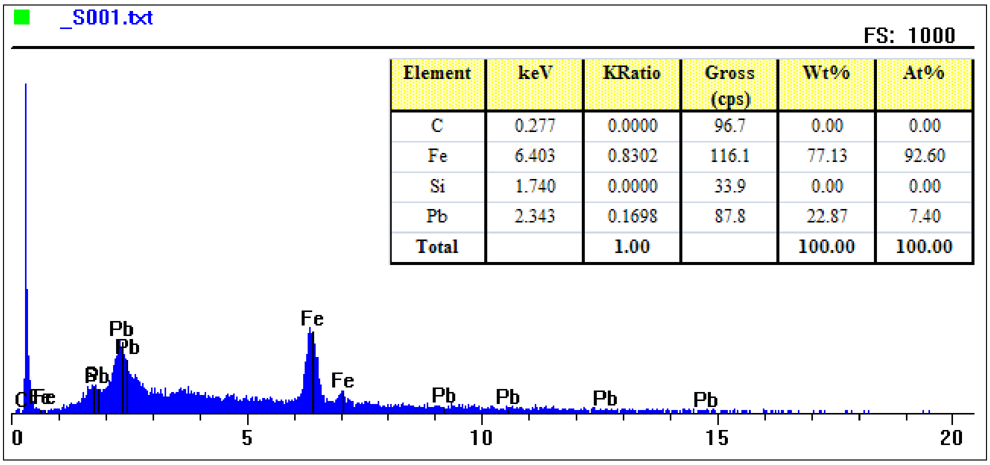
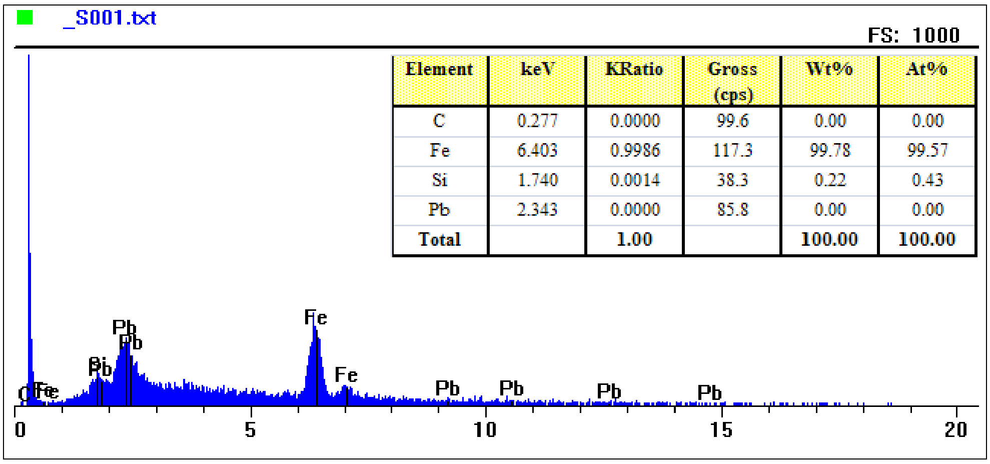
Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	106.3	0.00	0.00
Fe	6.403	0.8142	174.8	75.20	91.84
Si	1.740	0.0000	33.8	0.00	0.00
Pb	2.343	0.1858	83.6	24.80	8.16
Total		**1.00**		**100.00**	**100.00**

Figure 60. EDS spectrum of the Cleaner sample 1 area 1 (measured in Kev).



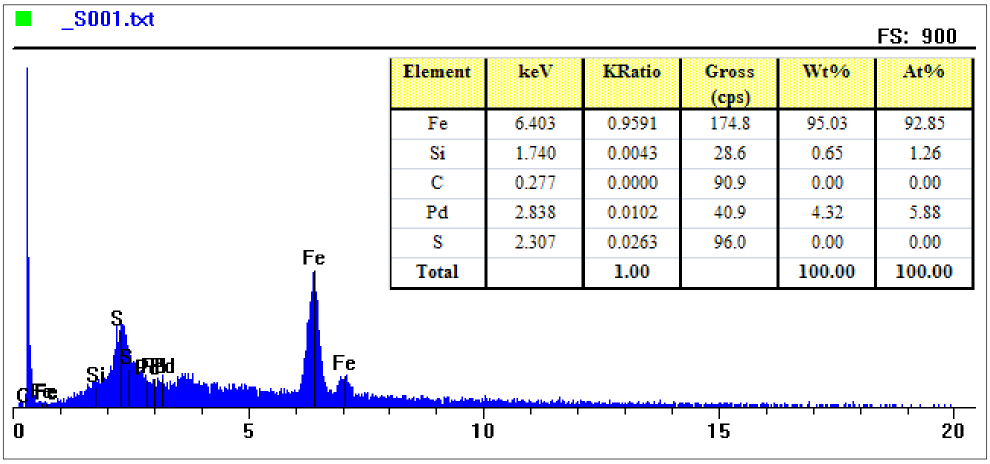
Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	96.7	0.00	0.00
Fe	6.403	0.8302	116.1	77.13	92.60
Si	1.740	0.0000	33.9	0.00	0.00
Pb	2.343	0.1698	87.8	22.87	7.40
Total		1.00		100.00	100.00

Figure 61. EDS spectrum of the Cleaner sample 1 area 2 (measured in Kev).



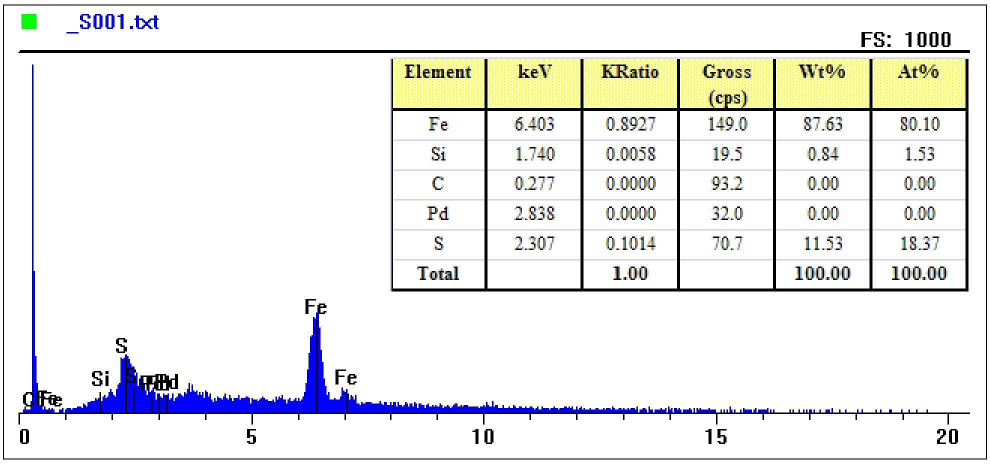
Element	keV	KRatio	Gross (cps)	Wt%	At%
C	0.277	0.0000	99.6	0.00	0.00
Fe	6.403	0.9986	117.3	99.78	99.57
Si	1.740	0.0014	38.3	0.22	0.43
Pb	2.343	0.0000	85.8	0.00	0.00
Total		1.00		100.00	100.00

Figure 62. EDS spectrum of the Cleaner sample 2 area 1 (measured in Kev)



Element	keV	KRatio	Gross (cps)	Wt%	At%
Fe	6.403	0.9591	174.8	95.03	92.85
Si	1.740	0.0043	28.6	0.65	1.26
C	0.277	0.0000	90.9	0.00	0.00
Pd	2.838	0.0102	40.9	4.32	5.88
S	2.307	0.0263	96.0	0.00	0.00
Total		1.00		100.00	100.00

Figure 63. EDS spectrum of the Cleaner sample 2 area 2 (measured in Kev).



Element	keV	KRatio	Gross (cps)	Wt%	At%
Fe	6.403	0.8927	149.0	87.63	80.10
Si	1.740	0.0058	19.5	0.84	1.53
C	0.277	0.0000	93.2	0.00	0.00
Pd	2.838	0.0000	32.0	0.00	0.00
S	2.307	0.1014	70.7	11.53	18.37
Total		**1.00**		**100.00**	**100.00**

Figure 64. EDS spectrum of the Cleaner sample 2 area 3 (measured in Kev).

Comparing the EDS data from the different treatments (Table 10) we verify the presence of elements such as Fe, S and Pb. These elements do not belong to any products used in the application of the alkoxysilanes technique, thus they probably correspond to a contamination which occurred during the impregnation process.

Analyzing the data of the weight content [Wt (%)] from the EDS analysis in the samples (Table 10) and when compared to the Control samples it appears the reduction of the silicone level in the samples is possible, either with the application of KNO_3 or Cleaner.

Table 10 – EDS Data of the samples in the different treatments.

Element (Wt %)	**Control**			**KNO_3**		**Cleaner**				
K				57.59	50.28					
Fe	40.42	40.98	46.30	31.52	37.22	91.84	77.13	99.78	95.03	87.63
C										
Na										
Si	2.20	2.99	2.31	1.36	1.25			0.22	0.65	0.84
Pb	57.38	56.03	51.39	9.53	11.25	8.16	22.87			
S									4.32	11.53
N										
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

22.3.6. Conclusions

Silicone oils are used to give a better structural capacity to the waterlogged organic materials, forming complex bonds with the cells tissue.

In this experiment, we tried to understand the effects of the KNO_3 and Cleaner in the samples treated previously (10 years ago) with alkoxysilanes (Control).

A reduction of the mass content of wood samples was verified when treatments to remove these polymers are used causing, what can be considered, a shrinkage phenomenon. It is confirmed by the statistical methods ANOVA and Duncan Test that the Cleaner treatment causes the higher mass loss and shrinkage process in both treenails samples, when compared with KNO_3 and Control.

Through the SEM micrograph it was possible to verify the collapse of the cell wall. Since it is common to all samples it cannot be attributed to the removal of polymer, but probably derives from an incorrect procedure of vacuum application, occurring 10 years ago, with the introduction of alkoxysilane into the wood structure.

Another analyzed feature was the presence of a high amount of white dots in the control samples when compared to the KNO_3 and Cleaner treatments. The EDS observations indicate a presence of foreign elements in the process, such as lead (Pb), iron (Fe) and sulfur (S), which probably derives from contamination which occurred during the impregnation with the silicone oils.

In the Control samples, the biggest content of silicon (Si)was observed, with the range between 2.20 to 2.99 % of the [Wt(%)], in the samples treated with KNO_3 the levels of Si are among 1.25 to 1.36 % and in the Cleaner samples the values are between 0.00 to 0.84 %.

Analyzing the data obtained with this experiment, we considered the possibility that the Cleaner from 3M^{TM} presents a superior ability to decrease the level of the silicon in the samples treated previously with alkoxysilanes, but at the same time causing the biggest physical shrinkage phenomena compared to the samples treated with KNO_3. Also it appears to be possible the application of the principle of removing silicon (Si) from alkoxysilanes in the environment rich in potassium, in this case with potassium nitrate.

For this reason we considered possible, in this particular case, the removing process of the cross-linked silicone oils from the wood samples, However it is necessary to carry out more studies to confirm these results and especially to give to the community a secure methodology process without destroying the artifacts structure.

CHAPTER VI – CONCLUSIONS

For many years, through the systematized study of physical remains and human marks on landscape, archaeological research was able to bring us knowledge about the course of civilization; clarifying social transformations and relationships that arose in societies, regardless of their temporal or geographic situation. In this "reconstruction work" the material cultural, that is, the evidence of the past, is responsible for offering specific data on historical and social contexts. However, contexts, artifacts and non-artifacts are worthless by themselves, and the way for them to be able to complement and consolidate knowledge is through archaeological interpretation. Therefore archaeological remains just support explanations. Nevertheless, they can be embedded with not only historical importance, but also can be considered aesthetically and socially important, visually and physically supporting the idea of cultural heritage.

Due to its important input, archaeology is seen as one of the essential disciplines that allows an understanding the past, and in so doing, also of the present. On the other hand, its role is not just being a part of the global process of knowledge about human experience, or of culture, it is also an element in the democratization development.

In the study of mankind, archaeology goes across every human trace, not being limited to land fieldwork, hence the research on submerged sites, maritime trade routes, coastal natural resources, inland settlements that can be reached by river, nautical transportation systems, or others. The research into this evidence reveals important historical and social information about everyday life, also indicating the degree of development of human relations. This is only possible since these contexts present a difficult access, which allows having deposits of artifacts and materials with a small amount of human interference.

Thus, most of the time, the underwater archaeologist is the person who during his discoveries, surveys or excavations, bring changes into the contexts. An underwater archaeological site is an ecosystem that once the elements in it are disturbed tends to degrade, until balance is achieved once again. Obviously, these changes are intrinsic to archaeological work, which does not mean that data relating to it will be lost. First, data will be kept through archaeological records; second, all actions performed by archaeological work can be minimized through conservation procedures.

The implementation of conservation procedures will make a difference, since the odds of materials surviving are much higher. Especially as regards the first archaeological approaches, such as excavations, or when materials are required to be studied on land, since these actions are those that have the biggest impact on the state of materials, once they are related to different environments.

Thus, considering the fact that these professionals are the ones responsible for exposure and the recovery of findings, within a practical perspective, they must be aware of the options in the safeguarding of materials. On the other hand, by understanding conservation features, they can also recognize characteristics about the materiality of objects, thus providing information to archaeology and from there to history. In this sense, conservation procedures are also able to link and to spread culture, and with it the role of history and, in particular, of archaeology, thus contributing to the development of knowledge of human civilizations. The recognition of the importance of these actions is not just emphasized by conservation itself, it also has an international paradigm recognized in all UNESCO conventions and recommendations, which once ratified at national level, must be performed as such.

To conserve underwater materials is mostly to preserve and to recognize the cultural heritage value of them, in such a way that communities are able to use them in the collective memory process. Therefore, underwater archaeology and conservation have a responsibility to the general public, which is respectively to present results of the research carried out, and to maintain the character and meaning of the cultural materials. Moreover, the audience is captivated by the historical facts and, at the same time, the awareness of these resources is raised.

Starting from this set of circumstances, we think that the work presented here did overcome the general difficulty of the understanding of the meanings of underwater organic cultural materials, their nature and preservation. Organic materials have been used since the beginning of human evolution, due to their easy access and properties. However, the last reason that made them so widely used is also the same reason that contributes to their degradation. So, due to their nature and as a consequence of physical, chemical and biological processes they are easily degraded. In order to maintain the information in them, their historic value and to permit access to these materials, specific treatments towards preservation can and must be performed.

Thus, after exploring the different natures of organic materials, leading to a better knowledge of the physical and chemical nature of materials, we made an approach to what we considered to be feasible treatments. In this sense, we performed the first Portuguese treatments of underwater organic materials with silicone oils, which were of major importance in the development of a new method, also introducing to the national panorama this "know-how", giving one more working tool to Portuguese underwater archaeologists and conservators, and thus adding value to this specialized work. In this study several major methods of conservation were presented, each one presenting pros and cons, and always bearing in mind that the selection of treatment will always depend on each particular case. The conservation of waterlogged organic materials is a challenge, which demands hard work, time and, sometimes, specialized equipment, but the advantages it brings to contemporary society are evident.

Despite the possible considerations and options, we believe that the best choices are *in situ* preservation, silicone oils and, still, PEG. *In situ* preservation allows direct contact with the archaeological reality, in its original context. This can lead to more benefits in terms of tourism, especially considering that underwater tourism is a growing economic area, capable of captivating audiences around the world, and that maritime and nautical museums or just museums with underwater archaeological materials attract many members of the public, which is also an opportunity to inform communities about the work done and the achieved results. On the other hand, the treatment of artifacts continues to be a very expensive process, and the monitoring necessary for the preservation of the site, although requiring special equipment is substantially less expensive than any laboratorial treatment. Including the monitoring, it can be carried out by the archaeologist, reducing even more the cost of hand work.

As for PEG, despite being a time consuming treatment, with strong probabilities that during treatment bacteria and fungi appear, as well as some sulfur compounds after treatment, it presents very good results at an aesthetic level, with reduced shrinkage and collapse. However, this treatment requires some experience or a specialized conservator.

During the last decades silicone oils have been successfully used in all kinds of materials. It is a simple procedure that is not so time consuming when compared with others. However, in Europe, its application is usually avoided except in extreme situations. This is due to the fact it is believed that alkoxysilanes are not removable. With our work, besides the study of the feasibility of silicone oil impregnation, we also question the hypotheses of its removal from materials. Starting with some wood samples we developed a method that can eliminate this product without harming the materials structure. So far, it seems possible to extract or remove the bonded alkoxysilanes. The analysis of the cell wall seems to be in good condition, so removal is possible without serious degradation of the wood structure. In our study we also analyzed the physical effects of silicone oil, noting that substantial changes occur in terms of weight, length and width. Despite the results, we think that further investigations are needed to better understand the behavior of reactions, and also to understand if it is possible to apply this method in other materials rather than wood.

Nevertheless, after the experiment we truly considered the silicone method as the most reasonable and possible to put into practice; first, because it does not require expensive equipment, second, because the procedure itself does not require much time to be concluded, finally no major needs of preventive conservation are required allowing access to materials, whether to be available to archaeological studies, or to be in an exhibition for viewing by the general public. This means really achieving the general goals of underwater archaeology and conservation.

The conservation treatments and preventive care measures described in this thesis illustrate the challenges within the discovery and recovery of underwater archaeological organic materials. The importance of these artifacts makes essential their conservation. However, these treatments are demanding and time consuming, so efforts to develop more effective actions must continue to be made.

The awareness of an underwater archaeologist of this kind of situations is vital, to be able to follow the materials from their original site, to his desk, until the lab and with proper safeguarding conditions this will improve the results of his work, as well as the conservation process. Achieving this aim will assist the archaeologist, both in the present, as in the future, to continue to extract data from it. Thus, this collaboration between disciplines will lead to better results in the quest for revealing our collective past.

Considering the geographic location of Portugal, its history of pioneering and seafaring, presuming that a great amount of Portuguese cultural heritage is still probably lying at the bottom of the oceans and seas, considering the importance of these remains for the understanding of our past, we believe that our work has contributed to archaeologists, scholars and the general public.

Nevertheless, the main goal of our thesis was to appeal to archaeologists to include conservation measures in the course of their work, giving them proper tools to be able to recognize the true chances of recovering underwater archaeological organic materials, evaluating and estimating the needs for each material, both in *in situ* preservation, as in the laboratory process, which will also reinforce the role of archaeology towards the cultural materials.

With this work we hope to collaborate on a new chapter in the Portuguese cultural scenario, since we believe that from the work presented here we can contribute to the knowledge about the course of civilization, preserving the traces from the past, which is our duty to safeguard and transmit to future generations, and thus benefiting the history and memory of Portugal.

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APPENDIX I - Statistical Analysis data from treenail 1

Descriptive Mass. Length and Thickness reduction

Treenail 1 - Treatments		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Mass (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	3.6633	0.45938	0.26523	2.5222	4.8045	3.14	4
	Cleaner	3	18.7467	0.41885	0.24182	17.7062	19.7871	18.49	19.23
	Total	9	7.47	8.61059	2.8702	0.8513	14.0887	0	19.23
Length (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	0.6667	0.24583	0.14193	0.056	1.2773	0.39	0.86
	Cleaner	3	2.4633	0.1365	0.07881	2.1242	2.8024	2.37	2.62
	Total	9	1.0433	1.11235	0.37078	0.1883	1.8984	0	2.62
Thickness (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	2.8867	0.86072	0.49694	0.7485	5.0248	1.92	3.57
	Cleaner	3	11.4767	0.76501	0.44168	9.5763	13.377	10.71	12.24
	Total	9	4.7878	5.20201	1.734	0.7892	8.7864	0	12.24

Test of Homogeneity of Variances in Mass. Length and Thickness reduction

Treenail 1 - Treatments	Levene Statistic	df1	df2	Sig.
Mass (%)	7.05	2	6	0.027
Length (%)	6.595	2	6	0.031
Thickness (%)	3.346	2	6	0.106

ANOVA in Mass. Length and Thickness reduction

Treenail 1 - Treatments		Sum of Squares	df	Mean Square	F	Sig.
Mass (%)	Between Groups	592.364	2	296.182	2299.16	0
	Within Groups	0.773	6	0.129		
	Total	593.137	8			
Length (%)	Between Groups	9.74	2	4.87	184.79	0
	Within Groups	0.158	6	0.026		
	Total	9.899	8			
Thickness (%)	Between Groups	213.835	2	106.917	241.882	0
	Within Groups	2.652	6	0.442		
	Total	216.487	8			

Mass reduction (%)

Treenail 1	Treatment	N	Subset for alpha = 0.05		
			1	2	3
Student-Newman-Keuls[a]	Control	3	0		
	KNO3	3		3.6633	
	Cleaner	3			18.7467
	Sig.		1	1	1
Duncan[a]	Control	3	0		
	KNO3	3		3.6633	
	Cleaner	3			18.7467
	Sig.		1	1	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Length reduction (%)

Treenail 1	Treatment	N	Subset for alpha = 0.05		
			1	2	3
Student-Newman-Keuls[a]	Control	3	0		
	KNO3	3		0.6667	
	Cleaner	3			2.4633
	Sig.		1	1	1
Duncan[a]	Control	3	0		
	KNO3	3		0.6667	
	Cleaner	3			2.4633
	Sig.		1	1	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Thickness reduction (%)

Treenail 1	Treatment	N	Subset for alpha = 0.05		
			1	2	3
Student-Newman-Keuls[a]	Control	3	0		
	KNO3	3		2.8867	
	Cleaner	3			11.4767
	Sig.		1	1	1
Duncan[a]	Control	3	0		
	KNO3	3		2.8867	
	Cleaner	3			11.4767
	Sig.		1	1	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

APPENDIX II – Statistical Analysis data from Treenail 2

Descriptive Mass. Length and Thickness reduction

Treenail 2 - Treatments		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Mass (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	4.85	0.25981	0.15	4.2046	5.4954	4.55	5
	Cleaner	3	16.6233	6.17435	3.56476	1.2854	31.9613	10	22.22
	Total	9	7.1578	8.02223	2.67408	0.9913	13.3242	0	22.22
Length (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	0.8833	0.47014	0.27144	0.2846	2.0512	0.42	1.36
	Cleaner	3	2.2667	0.69831	0.40317	0.532	4.0014	1.66	3.03
	Total	9	1.05	1.07523	0.35841	0.2235	1.8765	0	3.03
Thickness (%)	Control	3	0	0	0	0	0	0	0
	KNO3	3	1.6567	0.12583	0.07265	1.3441	1.9692	1.54	1.79
	Cleaner	3	9.1167	1.1692	0.67504	6.2122	12.0211	8.16	10.42
	Total	9	3.5911	4.2467	1.41557	0.3268	6.8554	0	10.42

Test of Homogeneity of Variances in Mass. Length and Thickness reduction

Treenail 2 - Treatments	Levene Statistic	df1	df2	Sig.
Mass (%)	6.299	2	6	0.034
Length (%)	3.524	2	6	0.097
Thickness (%)	8.622	2	6	0.017

ANOVA in Mass. Length and Thickness reduction

Treenail 2 - Treatments		Sum of Squares	df	Mean Square	F	Sig.
Mass (%)	Between Groups	438.469	2	219.235	17.222	0.003
	Within Groups	76.38	6	12.73		
	Total	514.849	8			
Length (%)	Between Groups	7.832	2	3.916	16.577	0.004
	Within Groups	1.417	6	0.236		
	Total	9.249	8			
Thickness (%)	Between Groups	141.51	2	70.755	153.496	0
	Within Groups	2.766	6	0.461		
	Total	144.275	8			

Mass reduction (%)

Treenail 2	Treatment	N	Subset for alpha = 0.05	
			1	2
Student-Newman-Keuls[a]	Control	3	0	
	KNO3	3	4.85	
	Cleaner	3		16.6233
	Sig.		0.147	1
Duncan[a]	Control	3	0	
	KNO3	3	4.85	
	Cleaner	3		16.6233
	Sig.		0.147	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Length reduction (%)

Treenail 2	Treatment	N	Subset for alpha = 0.05	
			1	2
Student-Newman-Keuls[a]	Control	3	0	
	KNO3	3	0.8833	
	Cleaner	3		2.2667
	Sig.		0.068	1
Duncan[a]	Control	3	0	
	KNO3	3	0.8833	
	Cleaner	3		2.2667
	Sig.		0.068	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Thickness reduction (%)

Treenail 2	Treatment	N	Subset for alpha = 0.05		
			1	2	3
Student-Newman-Keuls[a]	Control	3	0		
	KNO3	3		1.6567	
	Cleaner	3			9.1167
	Sig.		1	1	1
Duncan[a]	Control	3	0		
	KNO3	3		1.6567	
	Cleaner	3			9.1167
	Sig.		1	1	1

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.